

Dissociation as Measured by the Freezing
Point Lowering and by Conductiv-
ity---Bearing on the Hydrate Theory.
The Composition of the Hy-
drates Formed by a Number
of Electrolytes.

DISSERTATION

SUBMITTED TO THE BOARD OF UNIVERSITY STUDIES OF
THE JOHNS HOPKINS UNIVERSITY IN CONFORMITY
WITH THE REQUIREMENTS FOR THE DEGREE
OF DOCTOR OF PHILOSOPHY

BY

JAMES NEWTON PEARCE.

BALTIMORE

June, 1907

EASTON, PA. :
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Dissociation as Measured by the Freezing Point Lowering and by Conductivity— Bearing on the Hydrate Theory. The Composition of the Hydrates Formed by a Number of Electrolytes.

HISTORICAL.

The work of Arrhenius,¹ Raoult,² Loomis,³ Barnes,⁴ and of Jones and his co-workers⁵ upon the lowering of the freezing point of concentrated aqueous solutions of electrolytes show clearly that, starting with the most dilute solutions, the molecular lowering decreases, passes through a minimum and then increases with increasing concentration.

Conductivity measurements made by Jones and Knight,⁶ and Jones and Chambers,⁷ over the range of concentrations used in the above freezing point work showed no evidence of a minimum when the data were plotted in curves. Again, if we assume the dissociation as measured by the conductivity method to be correct as represented by $\alpha = \frac{\mu}{\mu_{\infty}}$, and from it calculate the theoretical molecular lowerings in each case, we find that these molecular lowerings decrease regularly, and, when plotted, show no evidence of a minimum.

It was from the work of Jones and Chambers that the first tentative suggestion was offered as to the cause of this phenomenon. Using their own words, it is this: "In concentrated solutions the salts must take up a part of the water, forming complex compounds with it, and thus removing it from

¹ Ztschr. phys. Chem., **2**, 496.

² *Ibid.*, **2**, 488.

³ Wied. Ann., **60**, 253 (1897); *Ibid.*, **57**, 503.

⁴ Trans. Roy. Soc. of Canada, Vol. VI., Sec. III., 37.

⁵ Ztschr. phys. Chem., **12**, 642. Am. Chem. Jour., **22**, 5 (1899). *Ibid.*, **22**, 110 (1899). *Ibid.*, **23**, 89 (1900). *Ibid.*, **23**, 512 (1900). *Ibid.*, **27**, 433 (1902). Ztschr. phys. Chem., **46**, 244. *Ibid.*, **49**, 385 (1904). Am. Chem. Journ., **31**, 303 (1904). *Ibid.*, **32**, 308 (1904). *Ibid.*, **33**, 534 (1904). Memoir Carnegie Inst., Washington, No. 60.

⁶ Am. Chem. Jour., **22**, 110 (1899).

⁷ *Ibid.*, **23**, 89 (1900).

the field of action as far as the freezing point lowering is concerned. This molecular complex, which is probably very unstable, acts as one molecule in lowering the freezing point of the remaining solvent. Thus the total amount of water present acting as solvent is equal to the total amount of water present diminished by that combined with the salt-molecules. By assuming that a molecule of the salt is in combination with a large number of molecules of water, it is possible to explain all of the freezing point results obtained.

"The conductivity results must, however, be taken into account. These show, unmistakably, a marked degree of dissociation even in the most concentrated solutions employed. There must be, therefore, a certain number of molecules broken down into ions, either by the water acting as a solvent or by the water in combination with the salt, just as salts are probably dissociated in their water of crystallization."

They also showed that in the concentrated solutions the molecular lowering is often much greater than the theoretical lowering, if all of the molecules were completely dissociated into ions. It is only on the assumption set forth by Jones and Chambers that this phenomenon can be explained.

Thinking that the hygroscopic property of certain substances might throw some light upon the point in question, Chambers and Frazer,¹ at the suggestion of Jones, took up the study of the freezing point lowerings produced by copper sulphate, phosphoric acid, hydrochloric acid, sodium acetate, cadmium iodide, zinc chloride, and strontium iodide, compounds with very great affinity for water. In all cases well defined minima were obtained, and from these minima the freezing point lowerings increased with increasing concentration, this substantiating the view put forth by Jones and Chambers.

Evidence for the Existence of Hydrates in Aqueous Solutions

1. *Relation between the Water of Crystallization and the Temperature at which the Salts Crystallize.*—If the assumption is true, that we are actually dealing with hydrates, un-

¹ Am. Chem. Jour., **23**, 512 (1900).

stable complex molecules of solvent and dissolved substance, then we should expect that the complexity of these hydrates would vary with the temperature, and with the existing conditions. That such is the case is proved by the fact that almost all of the water except that which is held as water of crystallization may be removed from solutions of salts at the boiling point of these solutions. Furthermore, the same results are obtained by spontaneous evaporation of the solvent from the solutions under reduced pressure at ordinary temperatures. What is still more striking, as we shall see in a subsequent discussion in this paper, is that these same molecular complexes may be broken down to some extent even in solution by the addition of a strong "dehydrating" agent. It is not to be assumed, however, that the resulting hydrate formed in the above three cases is the same. The very large number of cryoscopic measurements, which have been made in this laboratory, gives conclusive evidence that salts which crystallize with water of crystallization do combine with a much larger quantity of water when in solution at ordinary temperature.

If, then, the amount of water with which a salt can crystallize from a solution is a function of the temperature, we should expect this amount of water to be larger, the lower the water at which the crystals are formed.

We also have a class of substances which, under ordinary conditions, crystallize from solution without water of crystallization, *e. g.*, the chlorides of potassium and ammonium, and the nitrates of potassium, ammonium, sodium, and barium.

This is no doubt due, in some measure, to the temperature at which these substances have been allowed to crystallize. It is well known that conditions can be secured under which some of these substances separate from solution with small amounts of water of crystallization. It is still more probable, as we shall see later, that even the so-called anhydrous salts have considerable hydrating power in dilute solution.

2. Relation between the Water of Crystallization and the

Lowering of the Freezing Point.—An extensive investigation of the freezing point lowerings produced by aqueous solutions of electrolytes carried out by Jones and Getman,¹ and by Jones and Bassett,² has established the fact that there exists between the lowering of the freezing point and the water of crystallization this general relation; namely, that the magnitude of the freezing point lowering of a solution of any given electrolyte is directly dependent upon the number of molecules of water with which that salt crystallizes from solution.

A brief summary of this work, to which reference must be made to the curves in the original article, will bring out more clearly this relation.

If we consider the chlorides of the alkali group, all of which are binary salts, we find that the anhydrous salts, sodium chloride, potassium chloride, and ammonium chloride, give approximately the same depression of the freezing point with increasing concentration. Lithium chloride, with two molecules of water of crystallization, gives a considerably greater depression for the same concentrations.

The ternary chloride of calcium, strontium, magnesium, each of which crystallizes with six molecules of water, give depressions of the same order of magnitude, yet considerably greater than those of the alkali group. Barium chloride, with two molecules of water of crystallization, gives depressions lower than those produced by the other members of the alkali-earth group, yet greater than those produced by lithium with the same number of molecules of water of crystallization.

This is to be accounted for by the fact that lithium chloride is a binary electrolyte, yielding two ions while barium chloride is a ternary electrolyte yielding three ions. Again we find that the chlorides of iron, aluminium, and chromium, which separate from solution with six molecules of water, give much greater depressions of the freezing point than do

¹ Memoir Carnegie Inst., Washington, No. 60. *Ztschr. phys. Chem.*, **46**, 244 (1903); **49**, 385 (1904).

² *Am. Chem., Jour.*, **33**, 534 (1905); **34**, 290 (1905).

the chlorides of magnesium, calcium, and strontium. This is just what we should expect when we consider that the members of the iron group form quarternary salts while those of the alkali-earth group form ternary salts.

Similar relations are found to exist between the bromides, iodides, and nitrates of these metals.

If, however, we compare the molecular depressions produced the bromides and iodides of potassium, sodium and lithium, we find that in each case the sodium salts with two molecules of water give greater depressions than do the potassium salts crystallizing without water, yet smaller depressions than do the corresponding lithium salts crystallizing with three molecules of water.

Barium bromide, with two molecules of water of crystallization, shows a greater depression than does lithium bromide with three molecules, just as we should expect; it also gives a smaller lowering than do the bromides of calcium, strontium, and magnesium, each of which has six molecules of water of crystallization.

The nitrates of sodium, potassium, and ammonium, which crystallize without water, give the smallest lowerings of the freezing point, while lithium nitrate, with two molecules, comes next in the order of magnitude. About midway between lithium nitrate and those salts which crystallize with six molecules of water, lie the values for calcium nitrate, which has but four molecules of water.

The nitrates of aluminium, chromium, and iron crystallizing with eight and nine molecules, respectively, give the greatest lowerings of any salts so far studied. Comparing the chlorides, bromides, iodides, and nitrates of the alkali group which crystallize without water, we find that they all show a molecular lowering of the same order of magnitude for the dilute solutions, and this increases very slightly, if at all.

Lithium chloride and lithium nitrate, each crystallizing with two molecules, give approximately the same molecular lowerings. The same relation holds for lithium bromide and lith-

ium iodide, which crystallizes with three molecules. Further, the molecular lowerings produced by the nitrate and chloride are less than those produced by the bromide and iodide of lithium.

Owing to the slight solubility of barium chloride, comparisons between it and the bromide and iodide can be made only in dilute solutions. At these concentrations all three salts give molecular lowerings of approximately the same order of magnitude. In the more concentrated solutions the iodide gives a greater lowering than the bromide.

The chlorides, bromides, and iodides of the alkali-earths, which crystallize with six molecules of water, give lowerings of the freezing point which are of approximately the same order of magnitude. As in the case of the alkali metals, the bromides give somewhat greater lowerings than the chlorides, and the iodides still greater lowerings than the bromides.

The nitrates produce about the same lowerings as the corresponding chlorides which crystallize with the same number of molecules of water, and, therefore, somewhat less than the corresponding bromides and iodides.

In other words, if we consider in any one group those salts which separate from solution with the same number of molecules of water, we find that they produce molecular lowerings of approximately the same order of magnitude. If, on the other hand, the salts in the same group combine with varying amounts of water of crystallization, those salts having the greater combining power will produce the greater molecular lowerings, and *vice versa*.

Again, since the hydrating power is a function of the water of crystallization, the greater the number of molecules of water with which a salt crystallizes from solution, the greater will be the amount of water removed from the field of action as solvent, and, hence, the greater will be the abnormality in the freezing point lowering, due to this increase in concentration.

These facts give conclusive evidence of the truth of the theory advanced by Jones and Chambers¹ to account for the

¹ Am. Chem. Jour., 23, 89 (1900).

great abnormalities "that in solution the dissolved substance is combined with a part of the solvent, the amount of the solvent held in combination by the dissolved substance being a function of the concentration of the solution."

3. *Relation between the Minima in the Molecular Lowering of the Freezing Point and the Molecular Elevation of the Boiling Point.*—A short series of boiling point measurements was carried out in this laboratory by Jones and Getman.¹ They worked with aqueous solutions of potassium, sodium, lithium and barium chloride, potassium and sodium carbonates, and sodium sulphate.

In all cases slight but well-defined minima were obtained. These occur at somewhat greater concentrations than do the minima in the freezing point lowerings for the same electrolytes. That this is so is not surprising, since I have already pointed out that the complexity of the hydrates is decreased by increase in temperature. Hence, the amount of water removed from the field of solvent is less than at the freezing temperature. Therefore, a greater concentration is required in order that the effect due to hydration may counterbalance the effect due to decrease in dissociation.

4. *The Bearing of Hydrates on the Temperature Coefficient of Conductivity of Aqueous Solutions.*—The conductivity of a solution is, according to Ostwald, represented thus: $\mu_v = \alpha(c + a)$ when c and a represent the velocities of the cation and anion respectively, and α the dissociation at the given volume. Increase in conductivity may be brought about in two ways, either by increase in dissociation or by increasing the velocities of the ions.

It is a well-known fact that increase of temperature greatly increases the conductivity. Is this due to an increase in the velocity of the ions, or to an increase in dissociation? In an extended study of the temperature coefficients of conductivity in aqueous solutions, and on the effect of temperature on dissociation, it was found by Jones and West² that the

¹ Ztschr. phys. Chem., **46**, 244 (1903). Memoir Carnegie Inst., Washington, No 60, p. 12.

² Am. Chem. Jour., **34**, 357 (1905)

dissociation of electrolytes decreases slightly with rise in temperature between 0° and 35° . Noyes and Coolidge,¹ working at high temperature, have found that the dissociation decreases rapidly with rise in temperature. This is just what we should expect from our knowledge of the fact that the dissociating power of the solvent is a function of its own association. Since the association of the solvent decreases with increase in temperature, so should the dissociation of the electrolyte decrease, as has been found to be the case.

Since, then, we cannot attribute the increase in conductivity with rise in temperature to an increase in the dissociation of the electrolyte, we must conclude that the increase in conductivity with rise in temperature is due to an increase in the velocity of the ions.

The velocity of the ions depends first upon the driving power or kinetic energy, (2) upon the mass of the ion, and (3) upon the viscosity of the medium. It is a well-known fact that ions of small atomic masses move much more rapidly than those of higher atomic mass. Also, that increase in temperature of a given medium increases the kinetic energy of all particles in that medium. Increase in temperature also decreases the viscosity of the medium, thereby decreasing the "internal friction" of the ions.

All of these factors would increase the velocity with which the ions move, and, consequently, increase the conductivity as the temperature is raised.

Jones² has advanced another idea to account for the increase in conductivity with increase in temperature. "The mass of the ion decreases with rise in temperature. This does not refer to the charged atom or group of atoms which we usually term the ion, but to this charged nucleus plus a larger or smaller number of molecules which are attached to it, and which the ion must drag along with it through the remainder of the solvent.

"That the ions are hydrated seems to have been shown almost beyond question by Jones and his co-workers. That these hydrates are relatively unstable has also been demon-

¹ Ztschr. phys. Chem., **46**, 323 (1903).

² Memoir, Carnegie Inst., Washington, No. 60, p. 157.

strated; therefore, the higher the temperature, the less complex the hydrate existing in solution. The less the number of molecules of the solvent combined with the ion, the smaller the mass of the ion, and the less its resistance when moving through the solvent; consequently, the ion will move faster at the higher temperature.

"If this factor of diminishing complexity of the hydrate formed by the ion with rise in temperature, plays a prominent rôle in determining the large temperature coefficient of conductivity, then we should expect to find those ions with the largest hydrating power having the largest temperature coefficients of conductivity. The more complex the hydrate, *i. e.*, the greater the number of molecules of water combined with an ion, the greater the change in the complexity of the hydrate with rise in temperature."

Reference to the experimental data obtained by Jones and West¹ shows how well this idea is substantiated by the facts. To show this we give the following table. In the first column are given those salts which crystallize from solution with no water of crystallization and which, therefore, have but slight hydrating power in solution. In the second column are placed those salts which crystallize with large amounts of water, and which, consequently, have great hydrating power.

Substances with slight hydrating power.			Substances with large hydrating power.		
	Temp. coefficients in conductivity units.			Temp. coefficients in conductivity units.	
	$v = 2.$	$v = 1024.$		$v = 2.$	$v = 1024.$
NH ₄ Cl	2.07	2.94	CaCl ₂	3.11	5.61
NH ₄ Br	2.16	2.86	CaBr ₂	3.01	5.20
KCl	2.13	2.84	SrBr ₂	2.93	5.27
KBr	2.18	2.91	BaCl ₂	2.86	5.30
KI	2.09	2.91	MgCl ₂	2.55	4.59
KNO ₃	1.86	2.71	MnCl ₂	2.37	4.86
			Mn(NO ₃) ₂	2.24	4.16
			CoCl ₂	2.54	4.95
			Co(NO ₃) ₂	2.48	4.67
			NiCl ₂	2.63	5.04
			Ni(NO ₃) ₂	2.51	4.58
			CuCl ₂	2.15	5.04
			Cu(NO ₃) ₂	2.38	4.88

¹ Am. Chem. Jour., 34, 357 (1905).

From the points brought out in (1) we can assume, approximately, that the hydrating power of salts in solution is proportional to their water of crystallization. If this assumption is correct, we should expect to find that salts, having the same amounts of water of crystallization, *i. e.*, the same hydrating power, will have the same temperature coefficients of conductivity, and such we find to be the case. Further, the values of the temperature coefficients for a given concentration in either column are the same order of magnitude, those in the second column, in each case, being higher than the corresponding values in the first column, as we should expect from the greater hydrating power of the former. It will be seen that the temperature coefficients for $v = 1024$ are higher in every case than for $v = 2$, for each individual salt. The greater the dilution, the greater the complexity of the hydrate formed and the greater will be the change in the composition of the hydrate with change of temperature. Consequently, the temperature coefficient of conductivity is greater the more dilute the solution. Again, the differences in value between the temperature coefficients for $v = 2$ and $v = 1024$ is very much smaller in case of salts belonging to the first column than the corresponding differences for the salts of the second. In other words, the temperature coefficients of conductivity increase more rapidly with dilution for salts of greater hydrating power.

5. *The Absorption Spectra of Certain Colored Salts in Aqueous Solution as Affected by the Presence of Certain Other Salts with Large Hydrating Power.*—It has long been known that aqueous solutions of copper and cobalt halide salts, when treated with hydrochloric acid gas, calcium chloride, zinc chloride, aluminium chloride, and other strong dehydrating agents, undergo a change in color. Thus, when an aqueous solution of cobalt chloride is treated with a little solid calcium chloride or a concentrated solution of this salt, the initial purple-red color is changed to blue. Likewise, the green concentrated solution of cupric chloride, when diluted, becomes blue, and when the resulting solution is evaporated or treated with a dehydrating agent the original green color returns.

This change in color takes place regardless of the kind of substance used as a dehydrating agent. One particularly striking fact is this: the quantities of the dehydrating agents required to produce the same change in color are almost universally proportional to the number of molecules of water with which each salt crystallizes from solution.

A similar color change is met with if we heat to a high temperature solutions of colored electrolytes in sealed tubes. This phenomenon falls directly in line with the theory which has been advocated by Jones, that for each concentration of a solution of an electrolyte we have a definite molecular complex for a definite temperature, which breaks down with increasing temperature.

Many views have been put forth to explain these color changes. Jones and Uhler¹ undertook a spectrographic study of the absorption spectra of solutions of colored electrolytes.

The phenomenon of absorption is one of resonance. The waves have definite periods and definite amplitudes. If, now, these waves meet some medium containing particles which vibrate with the same or nearly equal periods, the energy of the wave is given up in setting the particle into vibration and the light is absorbed, as we say. We have the natural law that "that energy of vibration of a given period will be absorbed to the greatest extent by a system whose natural period of vibration is most nearly equal to its own." If the period of the vibration of the light wave differs appreciably from that of the system of particles, we shall have much less absorption.

If the mass of the vibrating particles, the hydrate, is increased by the addition of more water, while the energy of vibration remains the same, the period of vibration will be damped, and when tested, spectroscopically, the absorption bands will be found to grow smaller and smaller as the complexity of the hydrate increases.

If, on the other hand, we decrease the mass of the hydrate while the energy of vibration remains constant, the electrons

¹ Am. Chem. Jour., **37**, 126 (1907). Memoir, Carnegie Inst., Washington, No. 60.

in the hydrated molecule will vibrate in resonance with a larger number of ether waves, and the result will be that we will have a broadening of the absorption bands.

They first studied the absorption spectra of a series of aqueous solutions of cobalt chloride, copper chloride, and copper bromide.

They found that, with increase in concentration of the cobalt salt alone, the absorption bands widen out rapidly. This is just what we should expect from the results of the freezing point work. It has been found from this work that the hydration per molecule decreases with increase in concentration. In the dilute solutions we have the largest hydrates. These have small amplitudes and long periods, hence they will respond to fewer light waves. The result then should be a narrowing of the absorption bands, and such is found to be the case. On adding more of the salt it removes some of the water of the solution from the field of solvent, thus rendering the large hydrates which previously existed unstable under the new conditions. As a result, the former large hydrates break down into simpler forms, which will vibrate in resonance with a larger number of waves. The result is a widening of the absorption bands.

Jones and Uhler next added strong hydrating agents, such as calcium chloride and aluminium chloride, to other series of similar solutions of the same salts. On the basis of our theory the dehydrating agent will remove some of the water from the field as solvent, thereby producing the same effect as increasing the concentration of the colored salt alone.

A study of the spectrograms shows this to be the fact. Also keeping the concentration of the colored salt constant, as the concentration of the dehydrating agent is increased, the absorption bands broaden with marked regularity.

Spectrograms were made of these colored salts in solutions of ethyl and methyl alcohol, and acetone, also in binary mixtures of solvents in which water was the second solvent.

From the work of Jones and Getman¹ and Jones and Mac-

¹ *Am. Chem. Jour.*, **31**, 339 (1904).

Master¹ it was shown that these solvents do not possess any very great power to combine with salts in solution. This being the case, if we should take a solution of copper chloride in ethyl alcohol, the dissolved substance, forming no complex with the solvent, would be free to vibrate in resonance with a large number of wave lengths, and would, therefore, increase the width of the absorption bands. The spectrograms show wider bands than for aqueous solutions. As water was added in varying quantities the absorption bands became narrower, showing the damping effect due to increasing hydration.

Here, again, the facts most beautifully confirm the theory.

Before leaving this chapter we will sum up our evidence for the existence of hydrates in solutions of electrolytes.

1. In the case of all electrolytes there exists between the water of crystallization and the temperature at which the crystals are formed a definite relation which, under the same conditions, is constant for a given salt. With increasing dilution the molecules and ions of an electrolyte are able to take up a part of the solvent, forming unstable molecular complexes or hydrates.

For equivalent concentrations the complexity of the hydrates formed by different salts stands in close relation to the amounts of water with which those salts crystallize from solution.

2. The abnormality in the freezing point lowerings produced by solutions of electrolytes is a function of the water of crystallization of these electrolytes. Those salts which have a greater number of molecules of water of crystallization always produce the greater lowering of the freezing point. The same relation has been found to hold for the molecular rise of the boiling point.

3. The minima in the boiling point and freezing point curves occur at those concentrations at which the effect of hydration just balances that produced by a decrease in the dissociation of the electrolyte. Owing to the instability of the hydrates formed with rise in temperature, the minima

¹ Am. Chem. J., **35**, 316 (1906).

for the boiling point curves occur at greater concentrations than those for the freezing point curves.

4. The temperature coefficients of conductivity increase with increasing dilution. For salts which crystallize with the same amounts of water the temperature coefficients are of the same order of magnitude. Comparing salts which crystallize with different amounts of water, that one will have the largest temperature coefficient of conductivity which has the greatest power to combine with the solvent. In other words, the greater the power to bring water out of solution, as water of crystallization, the more complex will be the hydrate formed. The more complex the hydrate, the greater will be the temperature coefficient of conductivity.

5. The absorption bands produced by aqueous solutions of colored electrolytes widen with increase in concentration. The same effect is produced when an indifferent substance of strong dehydrating power is added. Similarly, increasing dilution, with its accompanying increasing hydration, decreases the width of the absorption bands.

Conductivity.

The conductivity of a solution of an electrolyte is a function of several conditions: the nature of the electrolyte and the degree of its dissociation; the speed of its component ions; and the viscosity of the solvent. The degree of dissociation, in turn, depends upon the concentration of the electrolyte and the nature of the solvent.

As was pointed out by Dutoit and Aston, that solvent whose molecules are associated to the greatest extent has the greatest dissociating power.

Weak acids, weak bases, and salts of weak acids and bases show constantly increasing dissociation with increasing dilution, but, within the limits of accuracy of our present methods, no maximum of conductivity is directly obtainable. On the other hand, strong electrolytes show rapidly increasing dissociation with slight increase in dilution—a maximum conductivity being reached at moderate dilution.

It is stated by Ostwald¹ that the anions of the halogen acids

¹ Lehrbuch, 2, 679.

move more rapidly than do those of the oxyhalogen acids, *e. g.*, $\overline{\text{ClO}_3}$, $\overline{\text{BrO}_3}$, $\overline{\text{IO}_3}$; that $\overline{\text{ClO}_4}$ has a greater migration velocity than $\overline{\text{IO}_4}$. In general, the more complex the ion, the slower its migration velocity. Especially is this the case with the anions of organic acids. With isomeric anions, however, the velocities are approximately equal. With increasing increments of CH_2 the velocity decreases regularly. The same may be said with regard to the organic cations.

It has been proved by Jones and Getman and by Loomis¹ that organic acids are not hydrated. It is clear that increase in ionic volume is accompanied by decrease in ionic speed, doubtless due to increase in friction between ion and solvent.

With this idea in mind, and with the evidence from the freezing point measurements that the ions form more and more complex hydrates with increasing dilution, we are forced to believe that the conductivities of solutions of strong electrolytes are less than they would be, theoretically, if there were no hydration, by an amount which is a function of the volume of the ionic complex.

Vollmer² determined the values of λ_∞ for solutions of potassium acetate, sodium acetate, potassium iodide, lithium iodide, lithium chloride, and silver nitrate, in water and alcohol. He found the relation $\frac{\lambda'_\infty \text{ alc}}{\lambda_\infty \text{ water}} = K = 0.33$ to hold in every case.

Kawalki³ found the same relation to exist between the speeds of diffusion of the same electrolytes in water and alcohol. It is of especial interest to note that the value which he obtained for his constant $\frac{D' \text{ alc}}{D \text{ water}} = K' = 0.33$ is the same as that found by Vollmer for conductivity. From their results we obtain the relation,

$$\lambda'_\infty : \lambda_\infty :: D' : D.$$

That this relation will hold, in case there is hydration or alco-

¹ Wied. Ann., **60**, 523 (1897).

² *Ibid.*, **52**, 328 (1894).

³ *Ibid.*, **52**, 300 (1894).

holation, is highly probable, since the resistance offered to the ionic complex will be the same in each case.

As stated by Jahn,¹ "recent measurements have made it probable that the mobility of the ions is not independent of their concentration, that they have greater mobility in more concentrated than in more dilute solutions." Reference to the work of Jones and Bassett² shows that this is just what we should expect. They found, by freezing point measurements, that the hydration per gram molecule of the electrolyte decreases, with increasing concentration, to a certain concentration corresponding to the minimum in the molecular lowering of the freezing point, and then decreases very slowly with increasing concentration. In the more concentrated solutions, then, we have smaller changes in hydration; therefore, smaller changes in the ionic volumes; hence, we should have smaller changes in the mobility of the ions.

That the conductivity depends, in no small degree, upon the viscosity of the solution has been known for a long time, yet the simultaneous action of the two conditions, dissociation and viscosity, renders it impossible to separate their effects. No simple relation exists other than that the conductivity decreases with increase in viscosity.

G. Wiedemann³ first called attention to the fact that the friction which the ions produce in their motion changes in the sense that the fluidity changes. Accordingly, the mobility of the ions should be a function of the fluidity of the solution.

That the conductivity does not depend exclusively upon the fluidity can be seen in the following case: A 1 per cent (by volume) solution of cane sugar and a 2.2 per cent solution of methyl alcohol have the same internal friction, *viz.*, 1.046, but the conductivity of potassium chloride in a 1 per cent sugar solution is decreased 3 per cent, while in 2.2 per cent methyl alcohol it is decreased 3.85 per cent.

Pissarjewski and Lemcke⁴ made the simple assumption that the conductivity is directly proportional to the disso-

¹ Grundriss der Electrochemie, p. 143.

² Am. Chem. J., **33**, 534 (1905).

³ Pogg. Ann., **99**, 228 (1856).

⁴ Z. physik. Chem., **52**, 479 (1905).

ciation, and inversely proportional to the viscosity, *e. g.*,
 $\mu = K \frac{\alpha}{\eta}$. At maximum dissociation $K = \mu_{\infty} \eta_{\infty}$. Therefore, the dissociation is $\alpha' = \frac{\mu_v \eta_v}{\mu_{\infty} \eta_{\infty}}$ and not $\alpha = \frac{\mu_v}{\mu_{\infty}}$.

In the dilutions which they used the K , calculated from $\alpha = \frac{\mu_v}{\mu_{\infty}}$, varies, while K , calculated from $\alpha = \frac{\mu_v \eta_v}{\mu_{\infty} \eta_{\infty}}$ is a constant.

The Object of This Investigation.

It was my plan in this work to study the relation between the dissociation as measured by the freezing point and conductivity methods; to determine to just what extent the conductivity of a solution is influenced by the hydration of the ions; and to study the effect of hydration upon the relative velocities of different ions.

Moreover, it was desired to test the reliability of the conductivity method as a means of measuring the dissociation of strong electrolytes.

In order to do this, it was found necessary to redetermine as accurately as possible the freezing point lowerings produced by various solutions of a large number of salts.

The object of the conductivity measurements was to determine the dissociation of the solution in question, as accurately as possible, in order that the theoretical lowering produced by the substance, if there was no hydration, might be calculated.

The freezing point measurements give us, on the other hand, an exact proportion between the number of dissolved particles, molecules, ions, or the hydrates of these, and the number of molecules of the solvent acting as such.

EXPERIMENTAL.

Freezing Point Apparatus.—For all concentrations from the most dilute up to those which could not be frozen by mixtures of salt and ice, a bath of rather large dimensions was used. The outer cylindrical vessel was made of heavy

galvanized iron—diameter 31 cm., depth 26 cm.—and covered on the outside by a heavy coat of felt to prevent radiation. Within this was a much smaller vessel of the same material with a tightly fitting cover. Soldered around the large hole in the center of the cover is a conical-shaped collar, which holds firmly the cork through which the thermometer is inserted. By this means the thermometer always reaches to the same depth in the solution. A second smaller hole in the side is provided for the passage of the stirrer. To the bottom and on the outside was soldered a short bolt, which, in turn, was screwed into a nut soldered to the center of the outer vessel. In this way firm support was given the inner vessel and danger of floating was avoided. The freezing tube proper was a large glass tube—length 17 cm., diameter 5.5 cm., and of 250 cc. capacity. It was supported within the smaller vessel at the bottom by a cork, and at the top by a cork ring which rested upon an iron ledge soldered to the inside of the small vessel. These dimensions allowed for an air space of about 2 cm. all around.

The stirrer consisted of a gold-plated brass disc with one large hole in the center to permit the passage of the thermometer, and around this smaller holes about 0.7 cm. in diameter.

Near the top of the large outer cylinder was soldered a small tube which served to keep the water in the bath at constant level.

By means of a bath of these dimensions the temperature of the freezing mixture could be kept constant for five or six hours. No attempt was made to control exactly the temperature of the bath, but experience taught us that only those freezing mixtures which required from forty seconds to one minute to cool the solution $0^{\circ}.1$ could be depended upon for reliable results.

For solutions requiring freezing mixtures of calcium chloride, the ordinary cryoscopic apparatus consisting of a battery jar, two test tubes were used.

For this work 4 thermometers of the Beckmann type were

employed, whose temperature ranges were $1^{\circ}.1$, $5^{\circ}.6$, $12^{\circ}.2$, and 25° . These were graduated into $0^{\circ}.002$, $0^{\circ}.01$, $0^{\circ}.02$, and $0^{\circ}.05$, respectively (whole scale). By means of a high-power lens it was easy to read to a tenth of the above graduations.

Conductivity.

Apparatus.—The conductivity measurements were made by means of the well-known Kohlrausch method, using the Wheatstone bridge, induction coil, and telephone receiver. The wire was calibrated according to the method of Strouhal and Barus.¹ The resistance coils were made by Leeds, of Philadelphia, and had been carefully calibrated.

Conductivity cells of two types were used. For the more dilute solutions cells of the type devised by Jones and Bingham² were employed. For the more concentrated solutions U-shaped cells, similar to those used by Jones and Getman,³ were found to be very convenient.

All conductivity measurements were made at 0° . For this purpose a small pail was filled with finely crushed ice, moistened with distilled water, and the cells packed into the ice as tightly as possible. The small pail was then placed in a spacious pan and the space between the pail and the pan filled with finely crushed ice.

Specific Gravity.

Since the solutions were made up at 20° , we thought it best to determine their specific gravities at the same temperature. The 20° bath was a large galvanized iron tub. By means of a very small flame below and a stirrer within, driven by a hot-air motor, the temperature could easily be kept to within $0^{\circ}.1$ of the desired temperature. Throughout this work six pycnometers of the Ostwald type were employed. They were carefully calibrated with pure redistilled water.

¹ Wied. Ann., **10**, 326 (1880).

² Am. Chem. J., **34**, 481 (1905).

³ Z. physik. Chem., **46**, 244 (1903).

Volumetric Apparatus.

The flasks and burettes used in this work were carefully calibrated at 20° by the method of Morse and Blalock.¹

Solutions.

Kahlbaum's "chemically pure" materials were used in every case and were further purified whenever it was thought desirable to do so. The method of preparing the solutions varied according to the solute employed. In general, a solution of slightly greater concentration than 2 normal was first made, and from this, by successive dilutions, the lesser concentrations were obtained. Whenever possible, the mother solution was made up by direct weighing; when the nature of the solute did not permit it to be weighed, the mother solution was diluted to convenient strength, and portions of the dilute solution were standardized either by gravimetric or volumetric methods.

Water.

The water which was used in all the solutions was purified according to the method of Jones and Mackay.² Ordinary distilled water was twice redistilled from an acidified solution of potassium dichromate, and the steam from the second distillation passed through a boiling solution of barium hydroxide. It had, at 0°, a conductivity of about 1.2×10^{-6} to 1.7×10^{-7} .

Calculation of the Composition of the Hydrates.

The method of calculating the amount of water combined with the dissolved substance is essentially the same as that used by Jones and Bassett.³ We have given the observed molecular lowering of the freezing point, the specific gravity of the solutions, and the dissociation. The observed molecular lowering is corrected for the difference between 1000 grams and the amount of water actually present in one liter of the

¹ Am. Chem. J., **16**, 479 (1894).

² *Ibid.*, **19**, 83 (1897).

³ *Ibid.*, **33**, 843 (1905); **34**, 298 (1905).

solution. This gives the true molecular lowering which would be produced by the substance at the dilution in question if there were 1000 grams of water present.

From the dissociation we calculate the true molecular lowering which would be produced by the dissolved substances if there were no hydration; and if there is no hydration these two values for the molecular lowering should be equal.

The calculated lowering, divided by the observed lowering and multiplied by 1000, gives the amount of water present playing the rôle of solvent, if the quantity of the substance present is dissolved in 1000 grams of water.

The difference between this amount of water and 1000 grams gives the amount of water which is combined with the dissolved substance in the solution in question.

Knowing the number of grams of water which are in combination with the dissolved substance, the number of gram molecules of water combined with the substance is obtained by dividing this number by 18. If we divide this value by the concentration in terms of normal, we obtain the number of molecules of water which are in combination with one molecule of the dissolved substance when the amount of substance present in one liter of the solution is dissolved in 1000 grams of water.

In the various tables of data the symbols have the following significance:

In the tables of freezing point measurements m is the concentration in terms of gram molecules per liter; Δ , the observed lowering of the freezing point, corrected for the separation of ice; Δ/m , the molecular lowering of the freezing point.

In the conductivity tables, V denotes the volume of the solution in liters which contains one gram molecular weight of the electrolyte; μ is the conductivity corrected for water; α is the approximate dissociation.

In the specific gravity tables, m is the concentration; W_{sol} , the weight of one liter of the solution; W_{salt} is the weight of the salt contained in one liter of the solution; and W_{H_2O} is the weight

of water contained in one liter of the solution. The percentage correction is the correction which must be applied to the freezing point lowering in order to refer it to 1000 grams of the solvent instead of the amount of water that is actually present in one liter of the solution in question.

In the hydrate tables, m is the concentration in gram molecules per liter; α , the approximate dissociation as measured by the conductivity method; L , the theoretical molecular lowering of the freezing point referred to 1000 grams of solvent; Δ/m , the observed molecular lowering; L' , the corrected molecular lowering; M , the number of gram molecules of water in combination with the solute; and H , the number of gram molecules of water combined with one molecule of the salt at the concentration in question.

Calcium Chloride.

The data for calcium chloride are given in Tables I. to IV.

The value of μ_{∞} is surprisingly low, when compared with that obtained by West¹ and by Bassett.² It is, however, very nearly equal to that obtained by Jones and Stine.³

A study of Table IV. leads us to the following conclusions: The theoretical molecular lowerings, as given in column L , decrease regularly with increase in concentration, while the corrected observed molecular lowerings, as seen in column L' , decrease rapidly, reach a minimum at 0.1 normal, and then increase with increase in concentration.

It is very probable that the value of L' for 0.01 normal is too large, but owing to the inaccuracy of the method for such dilutions, this is unavoidable.

It will be seen from column M that the amount of water which has entered into combination with the dissolved salt also passes through a minimum between 0.075 normal and 0.10 normal—the same concentration which gives the minimum molecular lowering of the freezing point. A similar minimum

¹ Am. Chem. J., **34**, 393 (1905).

² *Ibid.*, **33**, 547 (1905).

³ The article of Jones and Stine will be published in the American Chemical Journal in the near future.

was noted by Jones and Bassett¹ for concentrations ranging from 0.102 normal to 0.153 normal. It has been assumed hitherto, by Jones and his coworkers, that the minimum in the freezing point lowering always occurs in that concentration where the effect due to decrease in dissociation is just counterbalanced by the effect due to hydration. The values of L' and M also show that the abnormality of the freezing point lowering is greatly augmented by the relatively great hydrating power of the ions, since it is the ions with which we are chiefly concerned in the dilute solutions. A glance at column H shows us at once the great hydrating power of the ions in dilute solution. The values of H decrease regularly with increase in concentration to 0.10 normal. From that concentration on, the decrease in hydration is very slight as the concentration increases. In these concentrations the combined effect upon the freezing point lowering, due both to the dissociation and to the hydration of the ions, is small, compared with the effect due to the undissociated molecules.

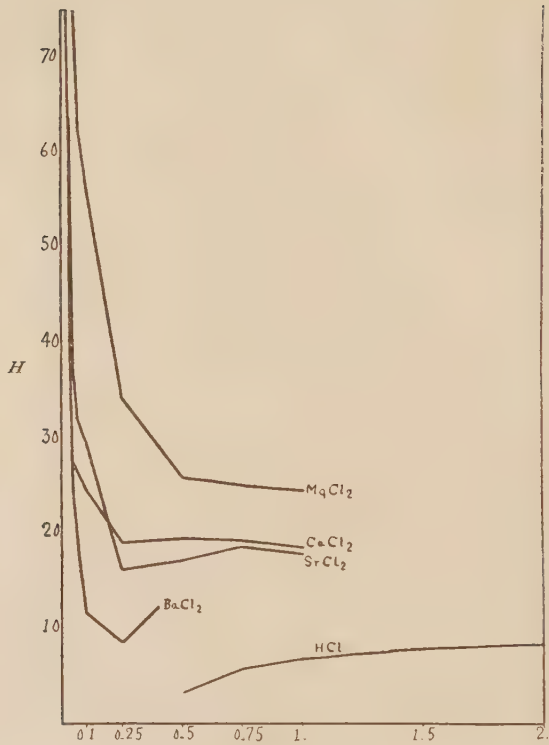
If we refer to the literature² bearing upon the relation between the water of crystallization of a salt and the temperature at which it crystallizes, we see that, over a definite range of temperature, the amount of water of crystallization is constant. If, then, we eliminate the hydration due to the ions, we should expect to find the number of molecules of water combined with one molecule of the salt to be a constant for a definite range of temperature. This is clearly shown by the values of H for the more concentrated solutions.

The values of M are plotted in the curve (Fig. II.) against the concentrations as abscissas. The curve shows, at a glance, that the amount of water held in combination, from the dilution at which the minimum occurs, is a linear function of the concentration.

The values of H are plotted in the curve (Fig. I.) against the concentrations as abscissas. An explanation regarding

¹ Am. Chem. J., **33**, 548 (1905).

² Bassett: *Ibid.*, **34**, 294 (1905).



Concentration.
Fig. I.

these hydrate curves is necessary at this point. With one or two exceptions, it was found impossible to plot on the paper the values of H for the more dilute solutions.

These curves show the rapid decrease in hydration until the minimum is reached, and then a very slight decrease with increasing concentration.

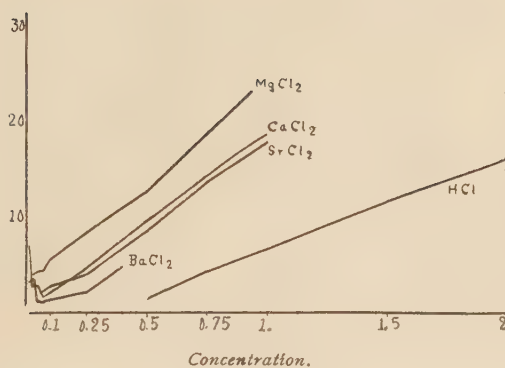


Fig. II.

Table I.—Freezing Point Measurements.

m .	Δ .	Δ/m .	i .	α .
0.01	0.05945	5.9450		
0.025	0.1318	5.2720	2.8344	91.72
0.05	0.2511	5.0220	2.7000	85.00
0.075	0.3651	4.8690	2.6177	80.88
0.10	0.48515	4.8515	2.6083	80.41
0.25	1.2335	4.9340	2.6526	
0.50	2.6270	5.2540	2.8247	
0.75	4.1955	5.5940	3.0075	
1.00	6.1040	6.1040	3.2817	

Table II.—Conductivity Measurements.

$$\mu_{\infty} 0^{\circ} = 123.46.$$

V .	μv .	α .
100	111.23	89.67
40	104.66	84.37
20	100.01	80.62
13.34	95.02	76.60
10	92.23	74.35
4	87.19	70.62
2	80.73	65.39
1.334	74.69	60.49
1.00	70.98	57.49

Table III.—Specific Gravity Measurements.

<i>m.</i>	Sp. gr.	<i>W</i> _{sol.}	<i>W</i> _{salt.}	<i>W</i> _{H₂O.}	Per cent of correction.
0.01	1.000982	1000.982	1.109	999.873	0.012
0.025	1.002539	1002.539	2.772	999.767	0.023
0.05	1.004874	1004.874	5.545	999.329	0.067
0.075	1.006814	1006.814	8.317	998.497	0.150
0.10	1.008971	1008.971	11.090	997.881	0.211
0.25	1.02267	1022.67	27.725	994.954	0.504
0.50	1.04451	1044.51	55.450	989.06	1.094
0.75	1.06641	1066.41	83.175	983.23	1.676
1.00	1.08744	1087.44	110.900	976.54	2.345

Table IV.—Hydrates.

<i>m.</i>	<i>α.</i>	<i>L.</i>	$\Delta/m.$	<i>L'</i>	<i>M.</i>	<i>H.</i>
0.025	84.37	4.9885	5.2720	5.2708	2.869	114.7
0.05	80.62	4.7590	5.0220	5.0187	2.874	57.4
0.075	76.60	4.7095	4.8690	4.8617	1.742	23.2
0.10	74.35	4.6258	4.8515	4.8414	2.474	24.7
0.25	70.62	4.487	4.934	4.910	4.785	19.1
0.5	65.39	4.293	5.254	5.197	9.663	19.3
0.75	60.49	4.110	5.594	5.501	14.048	18.7
1.00	57.49	3.998	6.104	5.962	18.30	18.3

Strontium Chloride.

The concentrated mother solution was diluted to convenient strength and equal portions were taken for standardization. The strontium was precipitated and weighed as strontium carbonate.

The conductivity measurements for this salt gave me, at maximum dissociation, $\mu_{\infty} = 128.57$. The corresponding value obtained by Jones and Stine¹ was $\mu_{\infty} = 128.44$.

The minimum in the freezing point lowerings (column *L'*) is found at 0.25 normal, whereas the minimum in the total combined water occurs at a somewhat greater dilution (0.05 normal). The values of *H* become approximately constant at 0.25 normal, the minimum point in the freezing point lowering.

The values of *m* and *H* for calcium and strontium chlorides Tables IV. and VIII., show numbers of approximately the same order of magnitude. For curves, see Figs. I. and II.

¹ *Loc. cit.*

Table V.—Freezing Point Measurements.

<i>m.</i>	Δ .	Δ/m .	<i>i.</i>	α .
0.01	0.05273	5.2730	2.8351	91.87
0.02937	0.1550	5.2800	2.8386	91.93
0.03987	0.2026	5.0752	2.7382	86.91
0.5011	0.2476	4.9349	2.6531	82.65
0.7077	0.3472	4.9060	2.6376	81.88
0.10	0.48904	4.8904	2.6292	81.46
0.25	1.1957	4.7830	2.5715	78.57
0.50	2.5339	5.0678	2.7354	
0.75	4.0989	5.4652	2.9385	
1.00	5.9211	5.9211	3.1833	

Table VI.—Conductivity Measurements.

$$\mu_{\infty} 0^{\circ} = 128.57 \text{ (Stine 128.4).}$$

<i>V.</i>	μv .	α .
1100	128.57	
550	127.99	
100	115.64	89.37
34.04	106.10	82.56
25.08	103.26	80.32
19.93	101.04	78.08
14.03	98.06	76.27
10	95.98	74.17
4	88.07	68.59
2	82.18	63.96
1.333	74.86	58.30
1.0	71.23	55.47

Table VII.—Specific Gravity Measurements.

<i>m.</i>	Sp. gr.	W_{sol} .	W_{salt} .	W_{H_2O} .	Per cent of correction.
0.01	1.0012284	1001.2284	1.585	999.7034	0.029
0.02937	1.0038396	1003.8396	4.6559	999.2837	0.071
0.03987	1.0053832	1005.3832	6.3197	999.0635	0.093
0.05017	1.007028	1007.028	7.952	999.078	0.092
0.07077	1.00956	1009.516	11.217	998.299	0.170
0.10	1.013205	1013.215	15.85	997.930	0.207
0.25	1.034433	1034.433	38.625	994.808	0.519
0.5	1.068379	1068.379	79.250	989.129	1.087
0.75	1.101760	1101.160	118.875	982.885	1.711
1.00	1.135423	1135.423	158.50	976.923	2.308

Table VIII.—Hydrates.

<i>m.</i>	<i>a.</i>	<i>L.</i>	$\Delta/m.$	<i>L'.</i>	<i>M.</i>	<i>H.</i>
0.01	89.37	5.1845	5.2733	5.2718		
0.02937	82.56	4.9312	5.2800	5.2763	3.634	123.6
0.03987	80.32	4.8479	5.0752	5.0705	2.439	61.2
0.05017	78.08	4.7645	4.9349	4.9304	1.871	37.2
0.07077	76.27	4.6982	4.9060	4.8977	2.274	32.13
0.10	74.17	4.6191	4.8904	4.8803	2.973	29.73
0.25	68.59	4.4115	4.7830	4.7582	4.047	16.18
0.50	63.96	4.2393	5.0678	5.0127	8.572	17.14
0.75	58.30	4.0287	5.4652	5.3718	13.890	18.52
1.00	55.47	3.9234	5.9211	5.7844	17.873	17.87

As in the case of calcium chloride, the values of the theoretical lowerings (*L*) are less than the observed lowerings (*L'*) in every instance.

Magnesium Chloride.

The value of μ_{∞} for magnesium chloride was found to be 123.95. The values of *L'* show a minimum at 0.25 normal, while the values of *H* begin to be constant at 0.5 normal. Magnesium chloride differs from the other chlorides thus far discussed in that its values for *M* show no minimum, but increase regularly with increasing concentration.

It should be noticed also that magnesium chloride has greater power to combine with water than any of the halides of the calcium group. Especially is this the case in the dilute solutions, where the ions predominate. That this is not due to hydrolysis and the liberation of the free mineral acid is evident from the fact that the molecular lowering of the freezing point in the dilute solutions is in every case considerably higher than the calculated lowering. As we shall see later, in our study of the acids just the reverse was found to be the case. The curves for this salt are found in Figs. I. and II

Table IX.—Freezing Point Measurements.

<i>m.</i>	Δ .	Δ/m .	<i>i.</i>	α .
0.004928	0.02741	5.5630	2.9909	99.54
0.007317	0.04072	5.5643	2.9916	99.58
0.01	0.05472	5.4720	2.9420	97.10
0.05108	0.2678	5.2443	2.8195	90.75
0.07171	0.3687	5.1421	2.7651	88.25
0.09986	0.5133	5.1330	2.7596	87.68
0.25	1.2352	4.9408	2.6563	82.81
0.50	2.6768	5.3536	2.8783	
0.75	4.4328	5.9104	3.1776	
0.9415	6.0619	6.4885	3.4615	

Table X.—Conductivity Measurements.

$$\mu_{\infty} 0^{\circ} = 123.95.$$

<i>V.</i>	μ_v .	α .
402.25	120.15	96.94
202.92	116.67	94.13
136.67	113.86	91.86
100.0	112.68	90.90
32.21	103.08	83.16
19.57	98.88	79.78
13.94	95.36	76.93
10.0	91.25	73.61
4.0	80.22	64.72
2.0	72.07	59.50
1.333	64.69	53.63
1.062	60.31	48.66

Table XI.—Specific Gravity Measurements.

<i>m.</i>	Sp. gr.	$W_{sol.}$	$W_{salt.}$	WH_2O .	Per cent of correction.
0.00493	1.000344	1000.344	0.4695	999.875	0.012
0.007327	1.000524	1000.524	0.6970	999.827	0.017
0.01	1.000842	1000.842	0.9526	999.889	0.012
0.03104	1.002756	1002.756	2.9568	999.799	0.020
0.05108	1.004224	1004.224	4.9168	999.307	0.069
0.07171	1.006036	1006.036	6.8316	999.204	0.079
0.100	1.008505	1008.505	9.5260	998.979	0.102
0.25	1.020966	1020.966	23.8150	997.151	0.284
0.50	1.038496	1038.496	47.630	990.866	0.910
0.75	1.056905	1056.905	71.445	985.460	1.450
0.9415	1.069617	1069.617	89.689	979.930	2.007

Table XII.—Hydrates.

<i>m.</i>	α .	<i>L.</i>	Δ/m .	<i>L'</i> .	<i>M.</i>	<i>H.</i>
0.01	90.90	5.2415	5.4720	5.4714	2.334	233.4
0.03104	83.16	4.9535	5.3581	5.3570	4.185	134.82
0.05108	79.78	4.8278	5.2443	5.2407	4.377	85.69
0.07171	76.93	4.7218	5.1421	5.1381	4.501	62.76
0.10	73.61	4.5982	5.1330	5.1278	5.737	57.37
0.25	64.72	4.1675	4.9408	4.9268	8.562	34.24
0.50	59.50	4.0734	5.3536	5.3049	12.898	25.79
0.75	53.63	3.8550	5.9104	5.8247	18.787	25.05
0.9415	48.66	3.6701	6.4385	6.3098	23.242	24.68

Barium Chloride.

A nearly saturated solution of this salt was first made. This was diluted to convenient concentration, and equal portions were precipitated and weighed as barium sulphate. Owing to the slight solubility of this salt, we did not attempt to work with concentrations greater than 0.4 normal.

Conductivity measurements gave us the value $\mu_{\infty} = 132.07$.

Table XIII.—Freezing Point Measurements.

<i>m.</i>	Δ .	Δ/m .	<i>i.</i>	α .
0.01	0.5463	5.4630	2.9370	96.85
0.025	1.3398	5.3592	2.8813	94.06
0.05	0.24770	4.9551	2.6639	83.19
0.075	0.36128	4.8171	2.5898	79.49
0.10	0.4792	4.7925	2.5766	78.83
0.25	1.1669	4.6677	2.5095	75.47
0.40	1.902	4.7370	2.5575	

Table XIV.—Conductivity Measurements.

$$\mu_{\infty} 0^{\circ} = 132.07.$$

<i>V.</i>	μ_v .	α .
100	120.01	90.87
40	111.15	84.16
20	105.78	80.09
13.33	100.69	76.24
10	99.92	75.65
4	92.18	69.79
2.5	86.31	65.35

Table XV.—*Specific Gravity Measurements.*

<i>m.</i>	Sp. gr.	$W_{sol.}$	$W_{salt.}$	$W_{H_2O.}$	Per cent of correction.
0.01	1.001878	1001.87	2.083	999.795	0.021
0.025	1.00475	1004.75	5.207	999.545	0.045
0.05	1.00929	1009.29	10.415	998.879	0.112
0.75	1.01369	1013.69	15.622	998.074	0.197
0.10	1.01766	1017.66	20.830	996.83	0.316
0.25	1.0456	1045.61	52.075	993.542	0.645
0.40	1.0726	1072.65	83.32	989.335	1.066

Table XVI.—*Hydrates.*

<i>m.</i>	$\alpha.$	$L.$	$\Delta/m.$	$L'.$	$M.$	$H.$
0.025	84.16	4.9907	5.3592	5.3568	3.796	151.8
0.05	80.09	4.8393	4.9551	4.9496	1.238	24.7
0.075	76.24	4.6961	4.8171	4.8080	1.293	17.2
0.10	75.65	4.6742	4.7925	4.7772	1.197	11.9
0.25	69.79	4.4562	4.6677	4.6374	2.172	8.69
0.40	65.35	4.2910	4.7570	4.7061	4.900	12.25

What has been said regarding the chlorides of calcium, strontium, and magnesium applies equally well to barium chloride. The low value of H for 0.25 normal is doubtless due to experimental error.

It is interesting to note that while the molecules of barium chloride have a much smaller hydrating power than the other chlorides of the alkaline earth metals, as we should expect from the fact that it crystallizes with but two molecules of water, the ions which predominate in the dilute solutions have a relatively high hydrating power.

Another point is to be noted, one to which reference will be made later in this paper. A glance at the curves representing the values of M and H for the three salts—calcium, strontium, and magnesium chlorides—will show that in each case the curves for calcium chloride lie above those for strontium chloride, while the two curves for magnesium chloride lie above those for calcium chloride. *This order is just the reverse of that for the atomic volumes of the three metals.* Although barium chloride crystallizes with but two molecules of water, the atomic volume of barium is still larger than that of strontium. This may account for the relatively high hydrating power of the ions of barium salts.

The curves for the values of M and H are given in Figs. II. and I., respectively.

Calcium Nitrate.

The mother solution was diluted and 50 cc. portions were taken for standardization. The calcium was precipitated by means of ammonium oxalate and weighed as calcium oxide. The data are given in Tables XVII. to XX.; the curves are plotted in Figs. III. and IV.

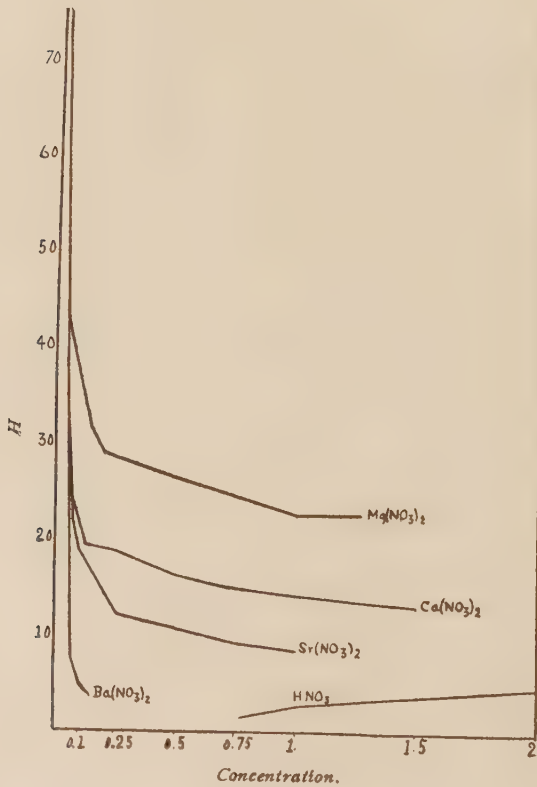


Fig. III.

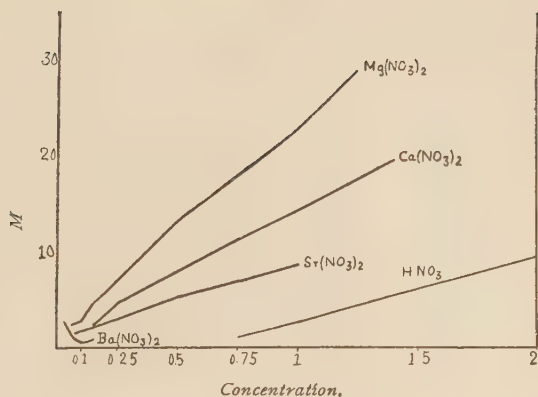


Fig. IV.

Table XVII.—Freezing Point Measurements.

m .	Δ .	Δ/m .	i .	α .
0.0125	0.072	5.7560		
0.025	0.1303	5.2120	2.8021	90.10
0.05	0.2405	4.8090	2.5855	79.27
0.125	0.5752	4.6019	2.4736	73.68
0.25	1.1424	4.5695	2.4567	72.83
0.5	2.2860	4.5720	2.4580	
0.75	3.484	4.645	2.4974	
1.0	4.766	4.766	2.5623	
1.5	7.616	5.077	2.7299	

Table XVIII.—Conductivity Measurements.

$$\mu_{\infty} 0^{\circ} = 126.69.$$

V .	μv .	α .
0.80	108.60	85.72
0.40	102.78	81.13
0.20	96.28	76.00
8.0	85.72	67.66
4.0	77.64	61.28
2.0	66.54	52.52
1.333	58.32	46.03
1.0	51.30	40.49
0.6667	40.24	31.75

Table XIX.—Specific Gravity Measurements.

<i>m.</i>	Sp. gr.	<i>W</i> _{sol.}	<i>W</i> _{salt.}	<i>W</i> _{H₂O.}	Per cent of correction.
0.0125	1.001846	1001.846	2.052	999.794	0.021
0.025	1.003166	1003.166	4.104	999.062	0.094
0.05	1.00604	1006.04	8.209	997.831	0.217
0.125	1.01523	1015.23	20.520	994.71	0.529
0.25	1.03074	1030.74	41.04	989.70	1.03
0.5	1.06011	1060.11	82.09	978.02	2.198
0.75	1.08874	1008.74	123.13	965.61	3.439
1.00	1.11751	1117.51	164.18	953.33	4.66
1.5	1.17375	1173.75	246.27	927.48	7.25

Table XX.—Hydrates.

<i>m.</i>	<i>α.</i>	<i>L.</i>	$\Delta/m.$	<i>L'</i>	<i>M.</i>	<i>H.</i>
0.025	81.13	4.8780	5.2120	5.2072	3.511	140.4
0.05	76.00	4.6872	4.8090	4.7986	1.288	25.7
0.125	67.66	4.3769	4.6019	4.5776	2.437	19.5
0.25	61.28	4.139	4.569	4.522	4.703	18.8
0.5	52.52	3.813	4.572	4.471	8.173	16.3
0.75	46.03	3.572	4.645	4.485	11.312	15.07
1.00	40.49	3.366	4.766	4.544	14.490	14.49
1.5	31.75	3.041	5.077	4.709	19.683	13.12

Nothing special need be said regarding the data for this salt, except to call attention to the fact that the amounts of water combined with calcium chloride in solution are, in general, higher than the amounts combined with calcium nitrate. This is just what we should expect when we consider that calcium chloride crystallizes with 6 molecules of water, while calcium nitrate crystallizes with 4.

Strontium Nitrate.

The strontium was precipitated and weighed as the carbonate. Unlike the other salts thus far studied, the freezing point lowerings show no minimum within the range of concentrations used, the molecular lowering constantly decreasing in value. A minimum was, however, obtained by Jones and Bassett¹ at a concentration of about 1.5 normal.

¹ Am. Chem. J., **34**, 305 (1905).

Table XXI.—Freezing Point Measurements.

<i>m.</i>	Δ .	Δ/m .	<i>i.</i>	α .
0.01	0.05717	5.7170	3.0736	103.68
0.025	0.1304	5.2180	2.8053	90.27
0.05	0.2402	4.8050	2.5833	79.16
0.075	0.3492	4.6567	2.5036	75.18
0.10	0.4587	4.5875	2.4664	73.32
0.25	1.0817	4.326	2.3263	66.31
0.5	2.0849	4.169	2.2418	62.09
0.75	3.0453	4.060	2.1829	59.15
1.00	3.9983	3.9983	2.1496	57.48

Table XXII.—Conductivity Measurements.

$$\mu_{\infty} 0^{\circ} = 125.62.$$

<i>V.</i>	μ_V .	α .
100	111.14	88.47
40	100.95	80.36
20	94.12	74.92
13.34	89.26	71.06
10	86.16	68.59
4	73.59	58.58
2	61.34	48.83
1.33	52.77	42.01
1	45.69	36.37

Table XXIII.—Specific Gravity Measurements.

<i>m.</i>	Sp. gr.	$W_{sol.}$	$W_{salt.}$	$W_{H_2O.}$	Per cent of correction.
0.01	1.001525	1001.525	2.116	999.409	0.059
0.025	1.004207	1004.207	5.292	998.915	0.108
0.05	1.008391	1008.391	10.584	997.807	0.219
0.075	1.012646	1012.646	15.876	996.77	0.323
0.10	1.016834	1016.834	21.168	995.666	0.433
0.25	1.04201	1042.01	52.92	989.09	1.09
0.5	1.08312	1088.12	105.84	977.28	2.27
0.75	1.12386	1123.86	158.76	965.11	3.48
1.00	1.16354	1163.54	211.68	951.86	4.814

Table XXIV.—Hydrates.

<i>m.</i>	α .	<i>L.</i>	Δ/m .	<i>L'</i> .	<i>M.</i>	<i>H.</i>
0.025	80.36	4.8493	5.7180	5.7124	3.870	154.8
0.05	74.92	4.6470	4.8050	4.7945	1.710	34.20
0.075	71.06	4.5034	4.6567	4.6418	1.657	22.09
0.10	68.59	4.4115	4.5875	4.5677	1.900	19.00
0.25	58.58	4.0391	4.3269	4.2798	3.124	12.49
0.5	48.83	3.676	4.169	4.075	5.437	10.87
0.75	42.01	3.422	4.060	3.918	7.030	9.37
1.00	36.37	3.213	3.998	3.806	8.607	8.65

The values for the combined water show a minimum at 0.075 normal, just as calcium nitrate does.

The hydration per ion and molecule also shows no tendency to become constant.

The curves are plotted in Figs. III. and IV.

Magnesium Nitrate.

The nitrate of magnesium, like the chloride, shows a much greater power to combine with water, throughout the range of concentration studied, than do the nitrates of the alkali earth metals.

Table XXV.—Freezing Point Measurements.

<i>m.</i>	Δ .	Δ/m .	<i>i.</i>	α .
0.02	0.1078	5.3903	2.8980	94.90
0.05	0.24968	4.9938	2.6848	84.24
0.10	0.49085	4.9085	2.6390	81.95
0.15	0.74486	4.9671	2.6705	83.52
0.20	0.99875	4.9937	2.6848	
0.50	2.74280	5.4856	2.9492	
1.00	6.5145	6.5145	3.5024	

Table XXVI.—Conductivity Measurements.

$$\mu_{\infty} 0^{\circ} = 119.90.$$

<i>V.</i>	μ_v .	α .
50	102.06	85.12
20	94.48	78.80
10	89.66	74.78
6.666	85.61	71.40
5	83.04	69.25
2	72.03	60.07
1	59.27	49.43

Table XXVII.—*Specific Gravity Measurements.*

<i>m.</i>	Sp. gr.	$W_{sol.}$	$W_{salt.}$	$W_{H_2O.}$	Per cent of correction.
0.02	1.00224	1002.224	2.968	999.255	0.074
0.05	1.005626	1005.626	7.422	998.204	0.179
0.10	1.011118	1011.118	14.844	996.274	0.372
0.15	1.016557	1016.557	22.266	994.291	0.571
0.20	1.022026	1022.026	29.688	992.338	0.766
0.50	1.054804	1054.804	74.220	980.584	1.941
1.00	1.107865	1107.865	148.440	959.425	4.057
1.274	1.136615	1136.615	189.112	947.502	5.249

Table XXVIII. *Hydrates.*

<i>m.</i>	$\alpha.$	$L.$	$\Delta/m.$	$L'.$	$M.$	$H.$
0.05	78.80	4.7913	4.9938	4.9849	2.157	43.14
0.10	74.78	4.6418	4.9085	4.8903	2.817	28.17
0.15	71.40	4.5161	4.9671	4.9388	4.759	31.73
0.20	69.25	4.4361	4.9937	4.9555	5.819	29.09
0.50	60.07	4.0946	5.4856	5.3792	13.260	26.52
1.00	49.43	3.6988	6.5145	6.2507	22.672	22.67
1.274	44.46	3.5139	7.1032	6.7303	29.006	22.76

The amount of water decreases with increase in concentration in the dilute solutions, reaches a minimum at 0.05 to 0.075 normal, and then increases regularly with increase in concentration.

The values of H do not approach a constant until normal concentration is reached.

It is very probable that the relatively low values of H for 0.05 and 0.1 normal are due to errors in measuring the freezing points of those solutions.

The curves for magnesium nitrate are given in Figs. III. and IV.

Barium Nitrate.

Owing to the very small solubility of this salt I did not attempt to make measurements beyond 0.15 normal. Barium nitrate has special interest in that it is the first salt thus far studied in this investigation which, under ordinary conditions, crystallizes without water.

Table XXIX.—Freezing Point Measurements.

<i>m.</i>	Δ .	Δ/m .	<i>i.</i>	α .
0.01	0.05545	5.5450	2.9812	99.06
0.025	0.12482	4.9928	2.6838	84.19
0.05	0.23281	4.6566	2.5035	75.18
0.075	0.32704	4.3606	2.3440	67.20
0.10	0.42018	4.2018	2.2590	62.95
0.15	0.59935	3.9955	2.1481	57.40

Table XXX.—Conductivity Measurements.

<i>V.</i>	μ_{∞}	α .
100	110.62	86.37
40	99.04	77.32
20	90.26	70.47
13.34	83.92	65.51
10	78.59	61.36
6.67	71.05	55.47

Table XXXI.—Specific Gravity Measurements.

<i>m.</i>	Sp. gr.	$W_{sol.}$	$W_{salt.}$	$W_{H_2O.}$	Per cent of correction.
0.01	1.002031	1002.031	2.14	999.891	0.088
0.025	1.005224	1005.224	6.537	998.687	0.131
0.05	1.010591	1010.591	13.074	997.517	0.248
0.075	1.015671	1015.671	19.611	996.060	0.394
0.10	1.021143	1021.143	26.148	994.995	0.500
0.15	1.031770	1031.770	39.222	992.548	0.745

Table XXXII.—Hydrates.

<i>m.</i>	α .	<i>L.</i>	Δ/m .	<i>L'</i> .	<i>M.</i>	<i>H.</i>
0.05	70.47	4.4814	4.6566	4.6451	1.957	39.15
0.075	65.51	4.2969	4.3606	4.3434	0.595	7.93
0.10	61.30	4.1425	4.2018	4.1808	0.509	5.09
0.10	55.47	3.9234	3.9955	3.9648	0.5805	3.87

It will be seen that, like strontium nitrate, the molecular lowering of the freezing point decreases regularly as the concentration increases, without showing a minimum value.

The amount of water held in combination decreases rapidly and reaches a minimum at 0.1 normal.

The hydration per molecule is very small, as we should expect, since the salt in its solid state is anhydrous. In the more dilute solutions, however, where the ions predominate, the hydration is of the same order as that of the other nitrates of the alkali earths.

This is, indeed, convincing proof that the ions themselves have great hydrating power.

It was pointed out in the introduction that if there were no hydration the corrected molecular lowering of the freezing point should be equal to the corrected lowering. A glance at Table XXXII. will show how closely the assumption agrees with facts. The values for the corrected freezing point lowerings for the three most concentrated solutions, in which the hydration is least, are only about one per cent higher than the calculated values. Moreover, if there is no hydration and if we may disregard the effect of viscosity upon the velocity of the ions, we should expect the dissociation as measured by the conductivity and freezing point methods to be the same. That this is true may be seen by consulting the values of α for 0.075, 0.10, and 0.25 normal in Tables XXIX. and XXX. Owing to slight hydration, the amounts of dissociation, as measured by the freezing point method, are slightly higher than those measured by the conductivity method.

The curves for barium nitrate are given in Figs. III. and IV.

Since the two barium salts studied are so slightly soluble, it was thought best to add the tables for the hydrates of barium bromide and barium iodide which were prepared by Jones and Bassett.¹ Both of these salts crystallize with two molecules of water of crystallization.

Table XXXIII.—Hydrates.

<i>m.</i>	α .	<i>L.</i>	Δ/m .	<i>L'</i>	<i>M.</i>	<i>H.</i>
0.10	79.3	4.81	5.06	5.04	2.54	25.4
0.15	77.7	4.75	4.91	4.88	1.48	9.9
0.25	73.8	4.60	5.00	4.96	4.03	16.1
0.40	71.3	4.52	5.09	5.03	5.63	14.1
0.50	68.8	4.42	5.18	5.09	6.22	12.5
0.6774	65.3	4.29	5.74	5.59	12.92	19.1
0.9032	64.8	4.27	5.87	5.66	13.64	15.1
1.1290	61.1	4.13	6.24	5.93	16.88	14.9
1.3548	58.4	4.03	6.66	6.28	19.90	14.7
1.5806	55.6	3.93	7.12	6.63	22.66	14.3
1.884	50.90	3.75	7.67	7.06	26.05	14.4
2.258	41.1	3.39	8.343	7.58	30.71	13.6

¹ Am. Chem. J., **33**, 553 (1905); **34**, 306 (1905).

Table XXXIV.—*Hydrates.*

<i>m.</i>	<i>α.</i>	<i>L.</i>	$\Delta/m.$	<i>L'.</i>	<i>M.</i>	<i>H.</i>
0.076	78.6	4.78	4.92	4.91	1.47	19.3
0.153	75.9	4.68	5.00	4.96	3.14	20.5
0.306	74.9	4.65	5.17	5.08	4.70	15.4
0.612	71.0	4.54	6.08	5.86	12.51	20.4
0.917	64.8	4.27	6.69	6.29	17.84	19.5
1.222	61.1	4.13	7.54	6.98	22.70	18.1
1.528	55.5	3.92	8.67	7.83	27.74	18.2
1.834	51.1	3.76	9.54	8.44	31.92	17.4
2.139	45.0	3.53	11.22	9.67	35.28	16.5

The solubilities of these two salts are nearly equal to that of the other halides of the calcium group. It is very probable, owing to the fact that Jones and Bassett used a thermometer less sensitive than the one employed in this work, that the observed freezing point lowerings for the most dilute solutions are too low. This would, of necessity, give low values for the total combined water and for the hydration.

The values of *M* for these salts increases regularly with increase in concentration. The magnitude of hydration for each salt is approximately constant. If we compare the values of *H* for the four barium salts in Tables XVI., XXXII., XXXIII., and XXXIV., we see that of the halides the iodide has the greatest hydrating power, and the chloride the least, while the bromide stands intermediate between the other two. The nitrate has the least hydrating power.

Since the chloride, bromide, and iodide crystallize each with two molecules of water, we should expect the observed molecular lowering to be greater than the calculated. Experimental results confirm this.

Cobalt Chloride.

An approximately two normal solution was first made up. A portion of this was diluted to convenient strength, and the cobalt determined electrolytically.

Cobalt chloride crystallizes with 6 molecules of water, and, like the other chlorides with the same amount of water of crystallization, has a large hydrating power. The results are just what we should expect.

Table XXXV.—Freezing Point Measurements.

<i>m.</i>	Δ .	Δ/m .	<i>i.</i>	α .
0.01	0.06241	6.241		
0.025	0.1394	5.5786	2.9992	99.96
0.05	0.2609	5.2186	2.8057	90.28
0.075	0.3356	5.1413	2.7641	88.20
0.10	0.5110	5.1100	2.7473	87.36
0.25	1.3040	5.2160	2.8043	
0.50	2.8371	5.6743	3.0507	
0.75	4.5860	6.1147	3.2874	
1.00	6.7157	6.7157	3.6105	
1.5	12.1308	8.0871	4.3532	
2.0	17.7342	8.8671	4.7672	

Table XXXVI.—Conductivity Measurements.

 $\mu_{\infty} 0^{\circ} = 117$ (Jones and Bassett)¹.

<i>V.</i>	μ_v .	α .
100	113.06	96.63
40	104.86	89.62
20	99.30	84.80
13.34	96.00	82.05
10	92.26	78.85
4	83.79	71.61
2	73.86	63.14
1.334	66.15	56.54
1	59.58	50.92
0.667	48.59	41.53
0.5	38.51	32.91

Table XXXVII.—Specific Gravity Measurements.

<i>m.</i>	Sp. gr.	$W_{sol.}$	$W_{salt.}$	$W_{H_2O.}$	Per cent of correction.
0.01	1.001159	1001.159	1.299	999.860	0.014
0.025	1.003052	1003.052	3.247	999.805	0.019
0.05	1.006065	1006.065	6.495	999.5703	0.043
0.075	1.009190	1009.190	9.7425	999.447	0.055
0.10	1.012386	1012.386	12.990	999.396	0.060
0.25	1.03049	1030.491	32.475	998.016	0.19
0.50	1.05492	1054.924	64.95	989.974	1.00
0.75	1.09118	1089.180	97.425	991.655	0.83
1.00	1.11847	1118.471	129.90	988.571	1.14
1.5	1.17502	1175.026	194.85	980.176	1.98
2.0	1.23637	1236.376	25.98	976.576	2.34

¹ Am. Chem. J., 33, 567 (1905).

Table XXXVIII.—Hydrates.

<i>m.</i>	α .	<i>L.</i>	Δ/m .	<i>L'</i> .	<i>M.</i>	<i>H.</i>
0.025	89.62	5.1938	5.5786	5.5776	3.822	152.88
0.05	84.87	5.0717	5.2186	5.2164	2.122	42.44
0.075	82.05	4.9122	5.1413	5.1385	2.444	33.68
0.10	78.85	4.7932	5.1100	5.1070	3.413	34.13
0.25	71.61	4.7098	5.2160	5.2057	5.292	28.31
0.50	63.41	4.2088	5.6743	5.6176	13.93	27.86
0.75	56.54	3.9632	6.1417	5.9937	18.22	25.09
1.00	50.92	3.7542	6.7157	6.6394	24.14	24.14
1.5	41.53	3.4049	8.0871	7.9270	31.69	21.1
2.0	32.91	3.0842	8.8671	8.6594	35.76	17.88

It will be noted, first of all, that the freezing point lowerings for all concentrations are greater than for any of the salts

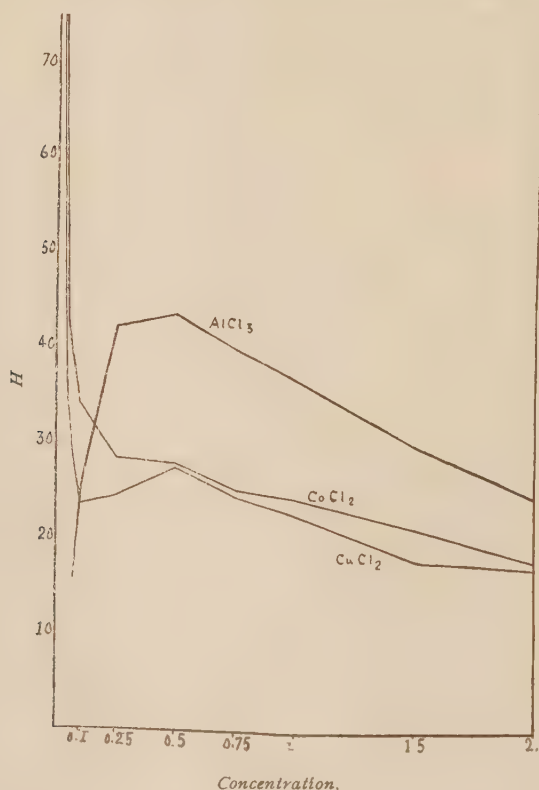


Fig. V.

thus far studied, and hence there is a correspondingly greater difference between the observed and calculated lowerings. The amount of water combined with the salt increases regularly from 0.05 normal to the most concentrated solution, as shown by Fig. VI. The hydration per molecule decreases rapidly in the most dilute solutions, and approaches a constant value at 0.25 normal. For the curve for hydrates, see Fig. V.

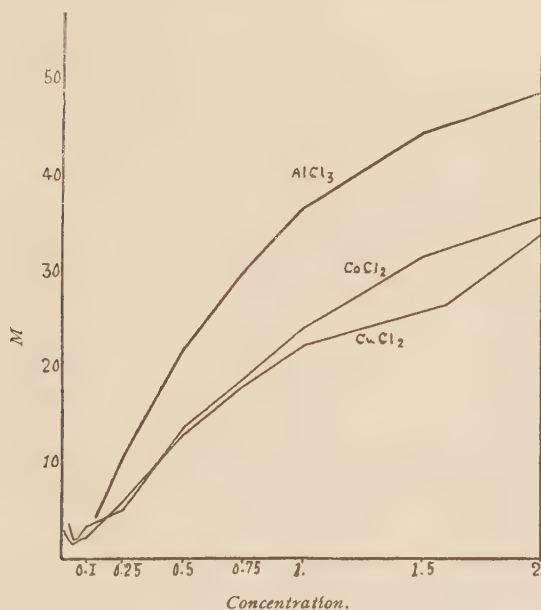


Fig. VI.

Cobalt Nitrate.

Cobalt nitrate, like cobalt chloride, crystallizes with 6 molecules of water, and we should expect it to have hydrating power of the same order of magnitude. The data given in the following tables show that such is the case. What has been said regarding cobalt chloride applies equally well to the nitrate.

The curves for the values of H and M are found in Figs. VII. and VIII., respectively.

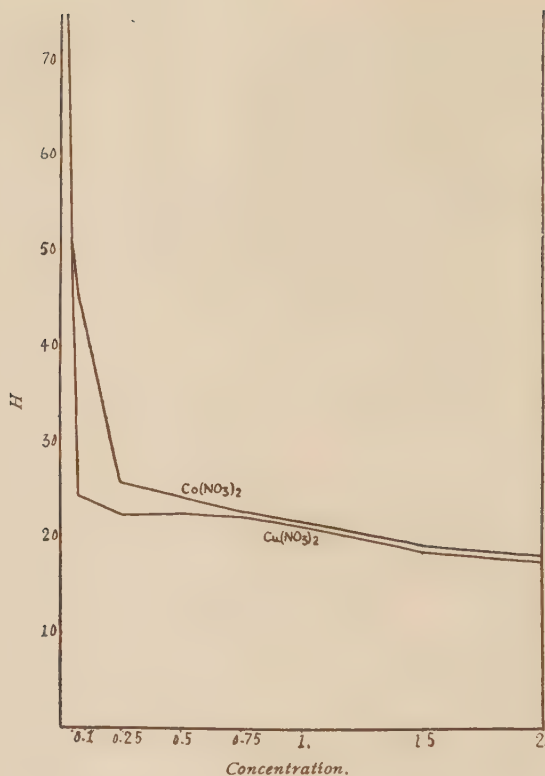
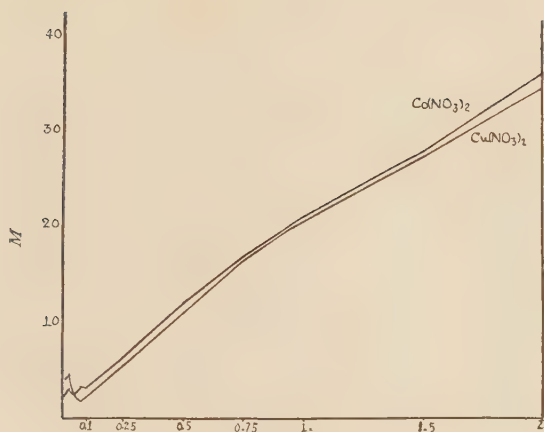


Fig. VII.

Table XXXIX.—Freezing Point Measurements.

<i>m.</i>	Δ .	Δ/m .	<i>i.</i>	α .
0.10	0.0553	5.5300	2.9731	98.65
0.025	0.1341	5.3640	2.8731	93.65
0.05	0.2572	5.1434	2.7652	88.26
0.075	0.3812	5.0826	2.7218	86.09
0.10	0.5005	5.0050	2.7096	85.48
0.25	1.2705	5.0082	2.7323	
0.50	2.708	5.417	2.9125	
0.75	4.338	5.784	3.1099	
1.00	6.220	6.220	3.3441	
1.5	10.888	7.192	3.8668	
2.0	18.863	9.431	5.0701	



Concentration.

Fig. VIII.

Table XL.—Conductivity.

$$\mu_{\infty} \text{ } ^{\circ} = 117.6.^1$$

<i>V.</i>	μ_v	α
100	108.66	92.40
40	100.69	85.62
20	96.12	81.73
13.334	91.67	77.95
10	89.94	76.48
4	81.48	69.28
2	72.94	62.02
1.333	65.32	55.54
1	58.89	50.08
0.668	47.57	40.45
0.5	37.10	31.55

Table XLI.—Specific Gravity Measurements.

<i>m.</i>	Sp. gr.	$W_{sol.}$	$W_{salt.}$	$WH_2O.$	Per cent of correction.
0.01	1.001496	1001.496	1.830	999.652	0.033
0.025	1.003863	1003.863	4.577	999.286	0.071
0.05	1.007579	1007.579	9.154	998.425	0.157
0.075	1.011289	1011.289	13.731	997.558	0.244
0.10	1.015084	1015.084	18.308	996.776	0.322
0.25	1.03737	1037.37	45.77	991.603	0.83
0.5	1.07415	1074.15	91.54	982.61	1.73
0.75	1.11204	1110.04	137.31	972.73	2.72
1.00	1.14612	1146.12	183.08	963.04	3.69
1.5	1.21720	1217.20	274.62	942.58	5.74
2.0	1.28576	1285.76	366.16	919.60	8.04

¹ Am. Chem. J., 33, 569 (1905).

Table XLII.—Hydrates.

<i>m.</i>	α .	<i>L.</i>	Δ/m .	<i>L'</i> .	<i>M.</i>	<i>H.</i>
0.025	85.62	5.0451	5.3640	5.3602	3.266	130.6
0.05	81.73	4.9003	5.1434	5.1354	2.544	50.8
0.075	77.95	4.7597	5.0826	5.0702	3.402	45.3
0.10	76.48	4.7050	5.0050	4.9889	3.161	31.6
0.25	69.28	4.437	5.082	5.0296	6.445	25.8
0.5	62.02	4.167	5.417	5.323	12.070	24.1
0.75	55.54	3.926	5.784	5.627	16.880	22.5
1.00	50.08	3.723	6.220	5.990	21.020	21.0
1.5	40.45	3.364	7.192	6.779	27.980	18.7
2.0	31.55	3.033	9.431	8.607	30.123	18.0

Copper Chloride.

Diluted portions of the mother solution were taken and the copper in them determined electrolytically.

While copper chloride crystallizes with two molecules of water, its power to combine with water is of the same order of magnitude as that of cobalt chloride and cobalt nitrate, as may be seen in the curves, Figs. V. and VII.

The total amount of water combined with the electrolyte passes through a minimum at about 0.05 normal and then increases rapidly with increase in concentration. This is seen in Fig. VI.

Table XLIII.—Freezing Point Measurements.

<i>m.</i>	Δ .	Δ/m .	<i>i.</i>	α .
0.01	0.05703	5.7030		
0.05	0.24944	4.9888	2.6821	84.10
0.075	0.37075	4.9433	2.6576	80.82
0.100	0.48665	4.8665	2.6164	
0.25	1.2237	4.894	2.6316	
0.50	2.669	5.338	2.8701	
0.75	4.245	5.661	3.0436	
1.00	5.994	5.994	3.2228	
1.50	10.105	6.737	3.6220	
2.0	15.294	7.647	4.1112	

Table XLIV.—Conductivity Measurements.

 $\mu_{\infty} 0^{\circ} = 120$ (Jones and Bassett).¹

V .	μv .	α .
100	110.55	92.12
20	95.88	79.98
13.34	93.27	77.72
10	90.21	75.17
4	80.20	66.83
2	69.08	57.56
1.334	61.03	50.86
1	54.01	45.00
0.6666	41.81	34.84
0.5	31.56	26.30

Table XLV.—Specific Gravity Measurements.

m .	Sp. gr.	W_{sol} .	W_{salt} .	W_{H_2O} .	Per cent of correction.
0.01	1.001208	1001.208	1.345	999.863	0.013
0.05	1.006370	1006.370	6.725	999.645	0.035
0.075	1.009264	1009.264	10.0875	999.176	0.084
0.10	1.012614	1012.614	13.450	999.164	0.263
0.20	1.030991	1030.991	33.625	997.366	0.263
0.50	1.051479	1061.479	67.25	994.229	0.57
0.75	1.090912	1090.91	100.87	990.037	0.99
1.00	1.120249	1120.24	134.5	985.749	1.42
1.50	1.177618	1177.61	201.75	975.868	2.41
2.0	1.234551	1234.55	269.0	965.55	3.44

Table XLVI.—Hydrates.

m .	α .	L .	Δ/m .	L' .	M .	H .
0.05	79.98	4.8352	4.9888	4.9871	1.693	33.85
0.075	77.72	4.7511	4.9433	4.9392	2.116	28.21
0.10	75.17	4.6563	4.8665	4.8695	2.354	23.54
0.20	66.83	4.3460	4.8949	4.8821	6.091	24.36
0.50	57.56	4.0012	5.3384	5.3076	13.67	27.34
0.75	50.86	3.7519	5.6611	5.5748	18.17	24.22
1.00	45.00	3.5340	5.9945	5.9088	22.33	22.33
1.50	34.84	3.1560	6.7370	6.5747	26.66	17.78
2.00	26.30	2.8383	7.6470	7.3836	34.20	17.10

¹ Am. Chem. J., **33**, 576 (1905).

Copper Nitrate.

The mother solution of the salt was diluted to convenient strength and the copper determined electrolytically.

Copper nitrate crystallizes with 6 molecules of water and, therefore, should give us hydration of the same order of magnitude as that found for the nitrate of cobalt and nickel, which crystallize with the same amount of water. Reference to Table L. will show that this is the fact. The minimum for the total amount of combined water is pronounced and lies between 0.075 and 0.25 normal. The hydration per molecule decreases rapidly with increase in concentration to 0.25 normal, and then becomes approximately constant.

The curves representing the values of H and M are given in Figs. VII. and VIII., respectively.

Table XLVII.—Freezing Point Measurements.

$m.$	$\Delta.$	$\Delta/m.$	$i.$	$\alpha.$
0.01	0.05736	5.7365	3.0841	
0.025	0.13852	5.5401	2.9785	98.92
0.05	0.25540	5.1081	2.7463	87.31
0.075	0.36979	4.9306	2.6508	82.54
0.25	1.221	4.885	2.6264	81.32
0.5	2.589	5.178	2.7841	
0.75	4.190	5.587	3.0039	
0.935	5.512	5.895	3.1696	
1.50	10.284	6.856	3.6861	
2.0	16.89	8.44	4.5419	

Table XLVIII.—Conductivity Measurements.

$\mu_{\infty} 0^{\circ} = 118.1$		
$V.$	$\mu_v.$	$\alpha.$
100	108.84	92.24
40	101.2	85.76
20	95.7	81.10
13.34	91.86	77.85
4	79.4	57.29
..	69.8	
1.334	62.0	52.54
1.0695	56.89	48.21
0.667	44.0	37.29
0.5	33.47	28.36

Table XLIX.—Specific Gravity Measurements.

<i>m.</i>	Sp. gr.	<i>W</i> _{sol.}	<i>W</i> _{salt.}	<i>W</i> _{H₂O.}	Per cent. of correction
0.01	1.001504	1001.5049	1.876	999.628	0.037
0.025	1.004076	1004.0764	4.692	999.384	0.061
0.05	1.007859	1007.8599	9.384	998.4759	0.152
0.075	1.011715	1011.7155	14.076	997.6395	0.236
0.25	1.040290	1040.2903	46.920	993.370	0.663
0.50	1.07723	1077.230	93.840	983.390	1.66
0.75	1.11469	1114.699	140.76	973.930	2.607
0.935	1.14262	1142.627	174.48	968.140	3.188
1.5	1.22618	1226.183	281.52	944.660	5.53
2.0	1.29262	1292.623	375.36	917.26	8.27

Table L.—Hydrates.

<i>m.</i>	α .	<i>L.</i>	Δ/m .	<i>L'</i> .	<i>M.</i>	<i>H.</i>
0.025	75.76	5.0502	5.5401	5.5368	4.882	195.2
0.05	81.10	4.8769	5.1081	5.1005	2.435	48.7
0.075	77.85	4.7560	4.9306	4.9188	1.839	24.5
0.25	67.29	4.363	4.885	4.852	5.607	22.4
0.50	59.15	4.060	5.178	5.092	11.261	22.5
0.75	52.54	3.814	5.587	5.441	16.612	22.15
0.935	48.21	3.653	5.895	5.708	19.953	21.3
1.50	37.29	3.247	6.856	6.447	27.575	18.38
2.0	28.36	2.914	8.44	7.749	34.65	17.32

Nickel Nitrate.

The nickel was determined electrolytically in diluted portions of the mother solution.

The hydrating power of nickel nitrate is of the same order of magnitude as that of cobalt and copper nitrates, which crystallize with the same amounts of water (see Fig. IX.). The total combined water passes through a minimum at 0.05 normal and then increases rapidly with increasing concentration (see Fig. X.).

Table LI.—Freezing Point Measurements.

<i>m.</i>	Δ .	Δ/m .	<i>i.</i>	<i>a.</i>
0.01	0.0550	5.5070	2.9607	98.03
0.025	0.1299	5.1960	2.7950	89.75
0.05	0.2487	4.9745	2.6744	83.72
0.075	0.3664	4.8854	2.6265	81.32
0.10	0.4960	4.9602	2.6667	
0.25	1.251	5.003	2.6901	
0.5	2.652	5.305	2.8524	
0.75	4.213	5.618	3.0205	
1.00	6.101	6.101	3.2801	
1.5	10.576	7.051	3.7910	
2.0	17.050	8.523	4.5334	

Table LII.—Conductivity Measurements.

$$\mu_{\infty} 0^{\circ} = 117.2.^1$$

<i>V.</i>	μ_v .	α .
100	106.77	91.10
40	100.31	85.58
20	93.57	79.83
13.34	89.74	76.77
10	87.84	74.94
4	80.07	68.31
2	71.44	60.95
1.334	64.06	54.65
1.0	57.38	48.95
0.667	45.79	39.06
0.5	35.61	30.38

Table LIII.—Specific Gravity Measurements.

<i>m.</i>	Sp. gr.	W_{sol} .	W_{salt} .	W_{H_2O} .	Per cent of correction
0.01	1.001521	1001.521	1.8278	999.693	0.030
0.025	1.003882	1003.882	4.5695	999.312	0.068
0.05	1.007792	1007.792	9.139	998.653	0.134
0.075	1.011541	1011.541	13.7085	997.029	0.216
0.10	1.015307	1015.377	18.278	997.029	0.291
0.25	1.03837	1038.37	45.695	992.68	0.732
0.5	1.07611	1076.11	91.390	984.72	1.527
0.75	1.11310	1113.10	137.08	976.01	2.39
1.0	1.14562	1145.62	182.78	962.88	3.71
1.5	1.22134	1221.34	274.17	947.17	5.28
2.0	1.29459	1294.59	365.56	929.03	7.09

¹ Am. Chem. J., **33**, 574 (1905).

Table LIV.—Hydrates.

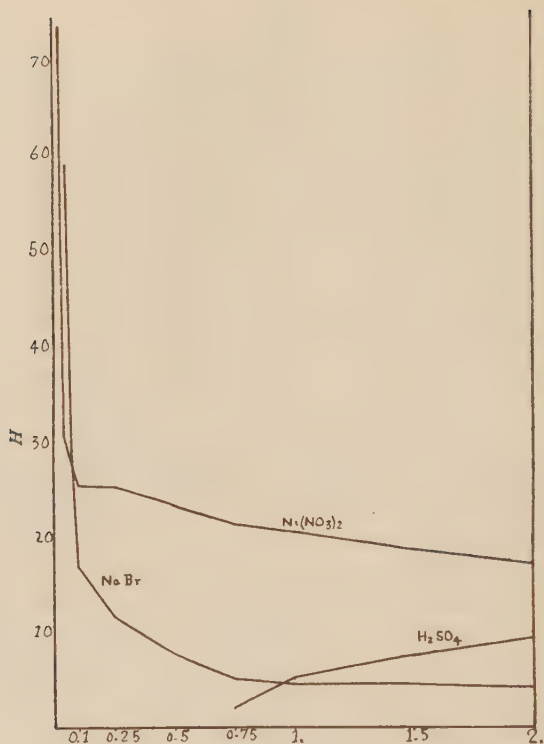
<i>m.</i>	α .	<i>L.</i>	Δ/m .	<i>L'</i> .	<i>M.</i>	<i>H.</i>
0.05	79.83	4.8296	4.9745	4.9679	1.545	30.9
0.075	76.0	4.7084	4.8854	4.8749	1.797	25.3
0.075	76.57	4.7084	4.8854	4.8749	1.897	25.3
0.10	74.94	4.6477	4.9675	4.8721	2.560	25.6
0.25	68.31	4.401	5.0036	4.9670	6.329	25.3
0.50	60.95	4.127	5.305	5.225	11.672	23.3
0.75	54.65	3.894	5.618	5.484	16.102	21.4
1.00	48.95	3.700	6.102	5.875	20.561	20.5
1.5	39.06	3.313	7.051	6.679	27.998	18.6
2.0	30.38	2.990	8.525	7.921	34.58	17.3

Before going farther, it will be interesting to note the great similarity between the salts of cobalt, copper, and nickel which we have just studied. Solutions of the same concentrations were used in all five salts.

Reference to Figs. VI., VIII., and X. will show at a glance the close relation between the amounts of water held in combination by these salts, whether they are chlorides or nitrates. We are not surprised at this, since, with the exception of copper chloride, all crystallize with 6 molecules of water. In fact, we found it impossible to put more than two curves on one sheet, so closely did the values agree. From the minimum in the most concentrated solutions studied, the magnitude of the hydrating power is a linear function of the concentration. In other words, each hydrate has its own definite composition, which varies with every concentration.

The curves representing the hydration per molecule (Figs. V., VII., and IX.) show the same striking similarity. They are almost asymptotic with the two coördinates. The hydration per molecule decreases very rapidly, for the very dilute solutions, to approximately the same concentration, when they become nearly constant for further increase in concentration.

Two conclusions are to be drawn from these relations. It will be noted that the molecular hydration and the total amount of water held in combination are the same for any two salts containing a common cation. It seems most probable that if the two anions, $\bar{\text{Cl}}$ and $\bar{\text{NO}}_3$, possess very different hydra-



Concentration.
Fig. IX.

ting power, this influence would manifest itself. It is a well-known fact that organic acids possess little or no hydrating power, and in the work which I have done upon the strong acids—hydrochloric, nitric, and sulphuric—this has been found to hold in the dilute solutions, where the dissociation is practically complete.

This would lead us to conclude that *the hydrating power of any salt is primarily a function of the cation.*

In the discussion of the nitrates and chlorides of the alkaline earth group, attention was called to the fact that the hydrating power of those salts is an inverse function of the atomic volumes.

In the case of the salts of cobalt, copper, and nickel which we have studied, we have to do with cations which have approximately the same atomic volumes.

As stated by Ostwald,¹ the migration velocity of an organic acid decreases with increase in the mass of the anion, as well as with increase in the mass of the cation in case of the organic bases. We should expect, then, to obtain larger values for conductivity than those given by the alkaline earth metals. Experiment shows the opposite to be the fact. We are, therefore, forced to believe that the effect of the atomic volume of the ions upon the conductivity is more than compensated for by the relatively large volume of the ionic complex.

Bredig² pointed out the fact that the migration velocities of elementary cations are a periodic function of the atomic weights. When plotted in a curve, where the ordinates represent velocities and the abscissas the atomic weights, it will be seen that the alkali metals lie very near the maxima of the curve, along with the halogens. At the extreme minima we find aluminium and chromium. Slightly above these lie the metals of the copper group, zinc, and cadmium; while still higher are to be found the metals of the alkaline earths.

The significance of this periodic relation between the migration velocities of the cations and the atomic weights has never been satisfactorily explained.

We believe that we have found the cause of this phenomenon. Of two ions or ionic complexes of different volumes, that one will meet with less friction on moving through the solution which has the smaller volume. Consequently, it will have the greater velocity. On the other hand, the greater the volume, the greater will be the friction to be overcome by the ion, and, hence, the smaller the velocity. Therefore, we should expect to find that those salts which crystallize with little or no water of crystallization give greater values for conductivity than those crystallizing with a greater amount.

It is a well-known law that the conductivity of an electrolyte depends upon the velocities of the ions. These velocities, in turn, depend upon the fluidity and the volume of the

¹ Lehrbuch, 2, 679.

² Z. physik. Chem., 13, 242 (1894).

ion. The greater the volume, the greater will be the resistance offered to the movement of the ions.

If we consider the alkalis we find that potassium, rubidium, and caesium, which have the largest atomic volumes and whose salts generally crystallize without water, have the greatest migration velocities, while lithium and sodium, which have smaller atomic volumes and whose salts crystallize with two or three molecules of water, have very much smaller migration velocities.

Comparing the members of the calcium group, we find that the atomic volumes increase with increasing atomic weight. The migration velocities of the cations calcium and strontium, whose salts usually crystallize with 6 molecules of water, are approximately equal to that of the barium cation, whose salts crystallize either with two molecules of water, or water-free. On the other hand, the magnesium cation, of smaller atomic volume, has a slightly smaller migration velocity, due to the more complex composition of its hydrates.

The cations of cobalt, copper, and nickel have approximately the same atomic weights, the same atomic volume, and the same hydrating power. Since these cations have the greatest hydrating power of any which we have studied, we should expect them to have the smallest migration velocities, and such is the case.

Aluminium Chloride.

Special interest is attached to the study of aluminium chloride, owing to the fact that it is a quaternary electrolyte and crystallizes with six molecules of water.

The hydrolytic effect of water upon this salt, in dilute solutions, can be noted in the first two concentrations. The hydrochloric acid liberated is almost completely dissociated at the dilutions in question, thus giving values for L which are considerably higher than would be obtained if the salt were not hydrolyzed. This may be attributed to one of two causes: the very high migration velocity of the hydrogen ion; its inability to form hydrates; or both. It is at about 0.075 normal that the influence due to the hydration of the aluminium cation begins to predominate. Just as we should ex-

pect, the number of molecules of water held in combination by one molecule of the electrolyte is large and increases very rapidly with increase in concentration (see Fig. VI.). In the curve representing the hydration per molecule (Fig. V.), that part representing concentrations between 0.075 and 0.5 normal represents the abnormality in the hydration due to hydrolysis.

A glance at column α (Table LVIII.) shows us that, in spite of the tendency of this salt to hydrolyze, the dissociation decreases very rapidly with increase in concentration. This is just what might be predicted. Its atomic volume is very small and the hydrating power of its cation very large. Therefore, it should have a very small migration velocity.

Table LV.—Freezing Point Measurements.

<i>m.</i>	Δ .	Δ/m .	<i>i</i> .	α .
0.01	0.712	7.1200	3.8279	94.26
0.025	0.1623	6.4940	3.4193	80.64
0.05	0.3053	6.1060	3.2827	76.09
0.075	0.4511	6.0153	3.2340	74.46
0.10	0.4511	6.0850	3.2704	
0.25	1.6604	6.641	3.5708	
0.50	3.9446	7.889	4.2415	
0.75	7.1339	9.511	5.1137	
1.00	11.795	11.795	6.341	
1.5	25.5 ¹	17.000	9.1398	
2.0	48.5 ¹	24.25	13.037	

Table LVI.—Conductivity Measurements.

<i>V.</i>	μ_{∞} 0° = 170. ² μv .	α .
100	156.48	92.04
40	141.24	83.08
20	130.44	76.72
13.334	126.66	74.50
10	122.07	71.80
4	106.90	62.88
2	88.60	52.11
1.333	75.02	44.12
1	61.93	36.42
1.6667	41.62	24.48
0.5	25.47	14.98

¹ These freezing points were determined by means of an alcohol thermometer and freezing mixtures of solid carbon dioxide and ether.

² Am. Chem. J., 31, 333 (1904).

Table LVII.—Specific Gravity Measurements.

<i>m.</i>	Sp. gr.	<i>W</i> _{sol.}	<i>W</i> _{salt.}	<i>WH</i> ₂ O.	Per cent of correction.
0.01	1.00104	1001.04	1.3345	999.71	0.029
0.025	1.00282	1002.82	3.3625	999.49	0.051
0.05	1.00588	1005.88	6.6725	999.21	0.079
0.075	1.00870	1008.70	10.0087	998.70	0.130
0.1	1.01158	1011.58	13.345	998.24	0.176
0.25	1.02911	1029.11	33.36	995.75	0.425
0.55	1.05706	1057.06	66.725	990.33	0.966
....	1.08431	1084.31	100.087	988.22	1.57
1.00	1.11054	1110.54	133.45	977.09	2.29
1.5	1.16308	1163.08	200.175	962.905	3.70
2.00	1.21378	1213.78	266.90	946.88	5.31

Table LVIII.—Hydrates.

<i>m.</i>	α .	<i>L.</i>	Δ/m .	<i>L'</i> .	<i>M.</i>	<i>H.</i>
0.01	92.04	6.9958	7.1200	7.1180		
0.025	83.08	6.4958	6.4940	6.4907		
0.05	76.72	6.1409	6.1060	6.1012		
0.075	74.50	6.0111	6.1526	6.1447		
0.10	71.80	5.8664	6.1560	6.1452	2.52	25.2
0.25	62.88	5.368	6.641	6.613	10.54	42.16
0.5	44.12	4.321	9.511	9.362	9.91	39.88
1.00	36.42	3.892	11.795	11.523	36.78	36.78
1.5	24.48	3.225	17.000	16.369	44.60	29.33
2.0	14.98	2.695	24.25	22.963	49.03	24.51

Sodium Bromide.

Dilute portions of the mother solution were standardized volumetrically by Volhard's method. This salt differs from those preceding in that it is a binary electrolyte and crystallizes with two molecules of water. A study of Table LXII. brings out the same general results. The observed molecular lowering passes through a minimum between 0.5 and 0.75 normal. The minimum in the total amount of combined water occurs at 0.10 normal. From the amounts of water which combine with one gram molecule of the salt, it will be seen that the sodium cation has nearly the same hydrating power in dilute solutions as do the cations of the calcium and copper groups.

The atomic volume of sodium is slightly more than half

that of potassium. Its hydrating power, however, for the more dilute solutions is much greater. If, then, the amount of hydration of the sodium ion is more than sufficient to compensate for the inverse volume relations, we should expect the migration velocity of sodium to be less than that of potassium. This has been found to be the case.¹

The atomic volume of sodium is also slightly less than that of calcium, and considerably less than those of strontium and barium; yet, owing to the greater hydration of the cations of the calcium group, its migration velocity is greater.

For the curves representing the values of H and M , see Figs. IX. and X.

Table LIX.—Freezing Point Measurements.

m .	Δ .	Δ/m .	i .	α .
0.01	0.03936	3.9360		
0.025	0.0952	3.8090	2.0478	104.78
0.05	0.1863	3.7260	2.0032	100.32
0.075	0.2727	3.636	1.9548	95.48
0.10	0.3572	3.572	1.9204	92.04
0.25	0.885	3.543	1.9049	90.49
0.50	1.787	3.574	1.9215	
0.75	2.696	3.595	1.9327	
1.00	3.633	3.633	1.9481	
1.5	5.654	3.769	2.0263	
2.00	7.746	3.873	2.0822	

Table LX.—Conductivity Measurements.

V .	μ_{∞} $0^{\circ} = 64.48$. ²	α .
	μ_v .	
100	61.12	94.78
40	59.02	91.53
20	57.67	89.44
13.334	56.33	87.36
10	55.28	85.73
4	51.08	79.21
2	49.51	76.78
1.333	49.06	76.08
1	47.61	73.83
0.6667	45.50	70.56
0.5	42.70	66.22

¹ Bredig: Z. physik. Chem., **13**, 242 (1894).

² Am. Chem. J., **34**, 375 (1905).

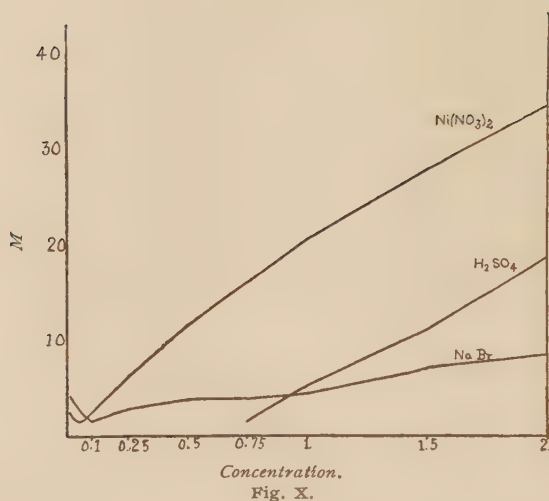


Table LXI.—Specific Gravity Measurements.

<i>m.</i>	Sp. gr.	<i>W</i> _{sol.}	<i>W</i> _{salt.}	<i>W</i> _{H₂O.}	Per cent of correction.
0.01	1.000732	1000.732	1.030	999.70	0.030
0.025	1.002177	1002.177	2.575	999.602	0.040
0.05	1.004074	1004.074	5.150	998.924	0.107
0.075	1.005972	1005.972	7.725	998.247	0.175
0.10	1.00788	1007.88	10.30	997.58	0.24
0.25	1.01964	1019.64	25.75	993.89	0.61
0.50	1.03908	1039.08	51.50	987.58	1.24
0.75	1.05811	1058.11	77.25	980.86	1.91
1.00	1.07632	1076.32	103.01	973.31	2.66
1.5	1.11963	1119.63	154.51	965.12	3.48
2.00	1.15240	1152.40	206.02	946.38	5.36

Table LXII.—Hydrates.

<i>m.</i>	<i>α.</i>	<i>L.</i>	<i>Δ/m.</i>	<i>L'</i>	<i>M.</i>	<i>H.</i>
0.025	91.53	3.5624	3.805	3.8075	3.575	143.0
0.05	89.44	3.5235	3.7260	3.7221	2.963	59.2
0.075	87.36	3.4848	3.636	3.6297	2.217	24.29
0.10	85.73	3.4545	3.572	3.5635	1.700	17.00
0.25	79.21	3.333	3.543	3.521	2.974	11.89
0.50	76.78	3.288	3.574	3.529	3.803	7.60
0.75	76.08	3.275	3.595	3.526	3.961	5.28
1.00	72.83	3.233	3.633	3.536	4.763	4.76
1.5	70.56	3.172	3.769	3.637	7.103	4.73
2.00	66.22	3.101	3.873	3.665	8.547	4.27

Hydrochloric Acid.

Having investigated fifteen salts, I next turned my attention to the study of some of the more common acids.

An approximately three normal solution of hydrochloric acid was prepared. Dilute portions of the mother solution were then titrated against a standard solution of potassium hydroxide free from carbonate. This, in turn, had been standardized by means of a tenth normal solution of freshly prepared oxalic acid. The results are given in Tables LXIII. to LXVI.

A glance at Table LXVI. shows that, for the more dilute solutions, the corrected observed freezing point lowering (L') is less than that calculated from the dissociation. This is due to one of two causes: the very high migration velocity of the hydrogen ion, or its inability to form hydrates.

The minimum in the freezing point lowering occurs at about 0.25 normal. For dilutions greater than 0.5 normal, there is no evidence of hydration. At 0.5 normal, however, the hygroscopic property of the molecular hydrochloric acid begins to predominate over the effect of decrease in dissociation. From this point the amount of combined water increases with increase in concentration. The corresponding values of H differ from those of the other electrolytes thus far studied in that they, also, increase as the concentration increases.

The values of H and M , for hydrochloric acid, are plotted in Figs. I. and II.

Table LXIII.—Freezing Point Measurements.

$m.$	$\Delta.$	$\Delta/m.$	$i.$	$\alpha.$
0.025	0.0902	3.6080	1.9377	93.97
0.05	0.1799	3.5980	1.9344	93.44
0.075	0.2681	3.5752	1.9221	92.21
0.10	0.3567	3.5670	1.9177	91.77
0.25	0.8862	3.5450	1.9059	90.59
0.50	1.841	3.682	1.9794	
0.75	2.852	3.804	2.0450	
1.00	3.975	3.975	2.1372	
1.50	6.452	4.301	2.3123	
2.00	9.367	4.683	2.5177	

Table LXIV.—Conductivity Measurements.

$$\mu_{\infty} 0^{\circ} = 236.92.$$

$V.$	$\mu_{v.}$	$\alpha.$
40	233.95	98.75
20	232.60	98.18
13.33	231.87	97.87
10	228.61	96.49
4	222.17	93.77
2	211.79	89.39
1.333	203.28	85.80
1	199.85	84.35
0.667	181.79	76.73
0.5	168.04	70.93

Table LXV.—Specific Gravity Measurements.

$m.$	Sp. gr.	$W_{sol.}$	$W_{salt.}$	$W_{H_2O.}$	Per cent of correction.
0.025	1.00034	1000.34	0.911	999.429	0.057
0.05	1.00101	1001.01	1.822	999.188	0.081
0.075	1.00135	1001.35	2.734	998.616	0.138
0.10	1.00180	1001.80	3.645	998.155	0.184
0.25	1.00425	1004.25	9.114	999.136	0.486
0.50	1.00849	1008.49	18.229	990.261	0.973
0.75	1.01264	1012.64	27.343	985.297	1.47
1.00	1.01749	1017.49	36.458	981.032	1.896
1.5	1.02542	1025.42	54.687	970.733	2.92
2.0	1.03414	1034.14	72.916	961.224	3.87

Table LXVI.—Hydrates.

$m.$	$\alpha.$	$L.$	$\Delta/m.$	$L'.$	$M.$	$H.$
0.025	98.75	3.6967	3.6080	3.6060		
0.05	98.18	3.6861	3.5980	3.5960		
0.075	97.87	3.6803	3.5752	3.5702		
0.10	96.40	3.6547	3.5670	3.5610		
0.25	93.77	3.6041	3.5450	3.5280		
0.20		3.5021	3.5310	3.6260	1.580	3.16
0.75	85.80	3.455	3.803	3.747	3.33	5.77
1.00	84.35	3.428	3.975	3.899	6.707	6.70
1.5	76.73	3.287	4.301	4.176	11.820	7.88
2.0	70.93	3.179	4.683	4.502	16.32	8.16

Nitric Acid.

A moderately concentrated solution was first made up, care having been taken that the acid used contained none of the oxides of nitrogen in solution.

Dilute portions of this were standardized volumetrically against a solution of potassium hydroxide.

Like hydrochloric acid, dilute solutions of nitric acid exhibit no tendency to form hydrates. No appreciable power to combine with water is manifested until the concentration 0.75 normal is reached. The amount of total combined water, then, increases with increase in concentration. The same results are obtained for the values of H . For curves representing the values of H and M see Figs. III. and IV.

Table LXVII.—Freezing Point Measurements.

$m.$	$\Delta.$	$\Delta/m.$	$i.$	$\alpha.$
0.025	0.09035	3.6140	1.9430	94.30
0.05	0.1791	3.5830	1.9263	92.63
0.075	0.2678	3.5713	1.9200	92.00
0.10	0.3547	3.5470	1.9069	90.69
0.25	0.8869	3.4576	1.9073	90.73
0.50	1.798	3.597	1.9341	
0.75	2.766	3.681	1.9736	
1.00	3.749	3.749	2.0156	
1.5	5.955	3.970	2.1344	
2.0	8.383	4.191	2.2532	

Table LXVIII.—Conductivity Measurements.

$$\mu_{\infty} 0^{\circ} = 237.07.$$

$V.$	μ_{25}	$\alpha.$
40	234.89	99.08
20	233.88	98.65
13.33	229.66	96.87
10	226.24	95.43
4	222.82	93.99
2	216.63	91.38
1.334	211.43	89.17
1.0	203.72	85.93
0.5	177.15	74.71

Table LXIX.—Specific Gravity Measurements.

<i>m.</i>	Sp. gr.	<i>W</i> _{sol.}	<i>W</i> _{salt.}	<i>W</i> H ₂ O.	Per cent of correction.
0.025	1.000926	1000.926	1.576	999.35	0.065
0.05	1.001798	1001.798	3.152	998.64	0.134
0.075	1.002653	1002.653	4.728	997.92	0.207
0.10	1.003496	1003.496	6.304	997.19	0.281
0.25	1.008481	1008.48	15.762	992.71	0.728
0.5	1.01686	1016.86	31.524	985.34	1.465
0.75	1.02503	1025.03	48.280	976.75	2.325
1.00	1.03360	1033.60	63.050	970.55	2.945
2.00	1.06700	1067.00	126.090	940.91	5.909

Table LXX.—Hydrates.

<i>m.</i>	α .	<i>L.</i>	$\Delta/m.$	<i>L'</i> .	<i>M.</i>	<i>H.</i>
0.025	99.08	3.7028	3.6140	3.6124		
0.05	98.65	3.6948	3.5830	3.5790		
0.075	96.87	3.6617	3.5713	3.5640		
0.10	95.43	3.6348	3.5470	3.5370		
0.25	93.99	3.6062	3.5476	3.5210		
0.5	91.38	3.559	3.597	3.544		
0.75	89.17	3.518	3.680	3.595	1.180	1.57
1.00	85.93	3.450	3.749	3.639	2.880	2.88
2.00	74.71	3.249	4.191	3.944	9.78	4.89

Sulphuric Acid.

Dilute portions of the mother solution were titrated against the standard potassium hydroxide used for the previous acids.

The results are given in Tables LXXI. to LXXIV.; the curves in Figs. IX. and X.

In dilute solutions no water is held in combination. The total amount of water held in combination by the acid, and the hydration per molecule, increases with concentration from 0.75 to 2 normal.

Table LXXI.—Freezing Point Measurements.

<i>m.</i>	Δ .	$\Delta/m.$	<i>i.</i>	α .
0.01	0.04872	4.8720	2.6193	80.96
0.025	0.1179	4.7184	2.5367	76.84
0.050	0.2182	4.3640	2.3462	67.31
0.075	0.3157	4.2099	2.2634	63.17
0.10	0.4043	4.0434	2.1738	58.69
0.25	0.9865	3.9460	2.1215	56.07
0.50	2.0033	4.0066	2.1541	
0.75	3.1174	4.156	2.2346	
1.00	4.379	4.379	2.3544	
1.50	7.265	4.843	2.6042	
2.0	11.296	5.648	3.0365	

Table LXXII.—Conductivity Measurements.

$\mu_{\infty} 0^{\circ} = 485.42.$		
<i>V.</i>	$\mu_v.$	$\alpha.$
100	398.34	82.06
40	353.41	72.80
20	335.56	69.13
13.34	323.43	66.63
10	314.42	64.78
4	296.30	61.04
2	281.52	57.99
1.334	271.25	55.88
1.00	259.05	53.37
0.6667	234.38	48.28
0.5	209.28	43.11

Table LXXIII.—Specific Gravity Measurements.

<i>m.</i>	Sp. gr.	$W_{sol.}$	$W_{salt.}$	$WH_2O.$	Per cent of correction.
0.01	1.000719	1000.719	0.980	999.74	0.026
0.025	1.001907	1001.91	2.451	999.45	0.054
0.05	1.003551	1003.55	4.902	998.65	0.135
0.075	1.005152	1005.15	7.353	997.79	0.220
0.1	1.00677	1006.77	9.807	996.97	0.303
0.25	1.01618	1016.18	24.51	991.67	0.832
0.5	1.03218	1032.18	49.03	983.14	1.68
0.75	1.04760	1047.60	73.53	974.07	2.59
1.00	1.06307	1063.07	98.07	964.99	3.50
1.5	1.09345	1093.45	147.11	946.34	5.36
2.0	1.12316	1123.51	196.15	926.99	7.30

Table LXXIV.—Hydrates.

<i>m.</i>	$\alpha.$	<i>L.</i>	$\Delta/m.$	<i>L.'</i>	<i>M.</i>	<i>H.</i>
0.01	82.06	4.9126	4.8720	4.8708		
0.025	72.80	4.5681	4.7184	4.7159		
0.05	69.13	4.4316	4.3640	4.3582		
0.075	66.63	4.3386	4.2099	4.2007		
0.10	64.78	4.2698	4.0434	4.0312		
0.25	61.04	4.1306	3.9460	3.9132		
0.5	57.99	4.017	4.266	3.939		
0.75	55.88	3.938	4.156	4.048	1.512	2.00
1.0	53.37	3.845	4.379	4.226	5.004	5.00
1.5	48.28	3.656	4.844	4.585	11.257	7.50
2.0	43.11	3.464	5.648 ¹	5.236	18.801	9.40

¹ Jones and Getman: Z. physik. Chem., 46, 272 (1903).

A comparison of Figs. I., III., and IX. shows that the hydrating powers of hydrochloric and sulphuric acids are of approximately the same order of magnitude, while that of nitric acid is slightly less.

Figs. II., IV., and X., representing the total amounts of combined water for the three acids, show that the same relation holds here as for the hydrates.

Discussion.

Fifteen salts and three strong acids have been studied in this investigation. I have worked with solutions covering a range of concentration from 0.01 to 2.0 normal; at one extremity are found to predominate, in a very pronounced manner, those influences due to the ions; at the other, those due to the molecules also manifest themselves. In this way I have attempted to compare the relative effects of the ions and the molecules upon the molecular lowering of the freezing point and the dissociation.

Comparing, first of all, the freezing point lowerings for any given solution, it is found that, without exception, the molecular lowering calculated from the dissociation decreases regularly with increasing concentration. Naturally, this follows from the fact that the decrease in dissociation is regular throughout. On the other hand, the corrected observed freezing point lowering decreases very rapidly in the dilute solutions, passes through a very pronounced minimum, and then increases as the concentration increases. A glance at the tables of the hydrates shows that in every case the observed molecular lowering produced by any salt is greater than the calculated lowering based on conductivity measurements.

If there were no hydration, we should expect the observed and the calculated molecular lowerings to be equal, except for the difference due to the influence of the friction between the ion and the solvent. The nearest approach to this condition which we have met is found in the most concentrated solutions of barium nitrate. Here the observed molecular lowering is about one per cent greater than the calculated value.

An equally satisfactory agreement was found by Jones and Stine for solutions of potassium chloride, which, likewise, crystallizes without water.

The values of M and H also show that the abnormality of the freezing point lowering in the dilute solutions is greatly augmented by the relatively great hydrating power of the ions.

Since, then, the hydration of the ion increases with increase in dilution, the volume and mass of the ionic complex is greater, the more dilute the solution; and, therefore, the greater will be the resistance to be overcome by the ion as it moves through the solvent. This being the case, the dissociation as measured by the conductivity method will be *less* than the true dissociation, and the abnormality in the dissociation measured will increase with increasing dilution.

The effect produced by adding more of the given electrolyte will be to break down these larger hydrates into simpler ones with smaller volume, thus decreasing the resistance to the motion of the hydrated ion.

This agrees well with the results of Jones and Uhler.¹ They found that the number of ether waves of different wave length with which a given particle will vibrate in resonance decreases with increasing dilution, thereby producing a narrowing of the absorption bands. On the other hand, the addition of more of the same electrolyte, or a strong dehydrating agent, decreases the complexity of the hydrate, thereby decreasing its period. As a result, the particles are free to vibrate in resonance with a greater number of wave lengths, and the absorption bands widen.

It will be seen that, with the exception of magnesium chloride, the value of M , the total amount of water held in combination by one molecule of the electrolyte, decreases rapidly in the dilute solutions, passes through a minimum, and then becomes a linear function of the concentration.

The hydration per molecule decreases rapidly, to approximately the same concentration which corresponds to a minimum in the freezing point lowering, and then remains practically constant as the concentration increases.

¹ Am. Chem. J., **37**, 126 (1907); Carnegie Inst. (Washington), Memoir No. 60.

Eliminating the hydration due to the ions, the hydration per molecule in solution over a given range of temperature is constant, just as the amount of water with which that same salt will crystallize from solution is constant for a given range of temperature. This relation is best illustrated by the curves representing the values of H . They are almost asymptotic to the coördinates.

Having found that the ions of a salt are hydrated, the next question which arises is this: Is it the cation or the anion which has the greater hydrating power?

Nernst, Garrard, and Oppermann,¹ in a study of the concentration changes which take place in an indifferent substance during electrolysis, have calculated that the ions $\overline{\text{SO}_4}$, $\overline{\text{Cl}}$, $\overline{\text{Br}}$, and $\overline{\text{NO}_3}$ drag with them 9, 5, 4, and 2.5 molecules of water, respectively.

It is seen from a study of the chlorides and nitrates of the copper group, each of which crystallizes with 6 molecules of water (copper chloride alone separating with two molecules), that the hydration per molecule is approximately the same for all of these salts. If, as Nernst and his coworkers have found, the hydrating power of the $\overline{\text{NO}_3}$ ion is only one-half that of the $\overline{\text{Cl}}$ ion, then we should expect the influence of the hydrating power of these two anions to manifest itself in the hydrating power of the salts in question, and especially so since the three cations are so nearly alike chemically. On the basis of this reasoning we are forced to conclude that the *hydrating power of any salt is primarily a function of the cation.*

We do not deny that the anions are capable of forming hydrates; but, if they do, experiments lead us to believe that they have this power only to a relatively slight degree.

We have noted also this striking relation. It is well known that if the atomic volumes of the elements are plotted as ordinates against the atomic weights as abscissas, there exists between them a periodic relation. At the maxima of the curve are the alkali metals. The three elements having the largest

¹ Göttingen Nachr., 1900, p. 86.

atomic volumes are potassium, rubidium, and caesium. Salts of these metals usually crystallize from aqueous solution in the anhydrous form, and as experiments have shown, they have very slight hydrating power in solution. Lithium and sodium, some of whose salts crystallize with two and three molecules of water, have much smaller atomic volumes.

At the minimum of the third section of the atomic weight curve we find the elements strontium, iron, cobalt, copper, and nickel. The salts of these metals crystallize with large amounts of water and show great hydrating power in solution. Aluminium, which has less than half the atomic weight of iron, but slightly greater atomic volume, lies at the second minimum. Its salts crystallize with 8 and 9 molecules of water and show great hydrating power in solution.

Comparing the metals of the alkaline earth group we find that barium, whose salts crystallize with two molecules of water or water-free, has the largest atomic volume. The other members of this group form salts which crystallize with 6 molecules, calcium nitrate excepted. The magnesium cation, which has the smallest atomic volume, has the greatest hydrating power in solution; the strontium cation, which has the largest atomic volume, has a smaller hydrating power than does the calcium cation, whose atomic volume is slightly less.

This is conclusive evidence that the *hydrating power of the cation is an inverse function of its atomic volume.*

That the velocities of the ions are an inverse function of their mass (and perhaps of their volumes) is an established fact. Experimental evidence, however, seems at variance with this statement. We should expect those ions which have the smallest atomic volumes to have the greatest migration velocities. On the contrary, we find that potassium, rubidium, and caesium have the greatest migration velocities (H^+ and OH^- excepted), while the ions of the iron and copper groups, with very small atomic volumes, have the smallest migration velocities.

A glance at the two curves representing the relation between atomic volume and atomic weights, and between migra-

tion velocities and atomic weights, shows at once the cause of this apparent anomaly. It has been shown that those elements which have the smallest atomic volumes have the greatest hydrating power, and *vice versa*. We see, then, that *those ions which have the smallest migration velocities have also the greatest hydrating power.*

A somewhat detailed comparison of the members of the different groups will bring out this idea more clearly.

The atomic volumes of potassium, rubidium, and caesium increase rapidly with increasing atomic weights, and, as a rule, their salts crystallize without water. We should expect, then, the potassium ion to have the greatest migration velocity, and the caesium ion to have the smallest. Experiments show that they have approximately the same migration velocities. Sodium and lithium, whose atomic volumes are less than half that of potassium, have migration velocities which are only about two-thirds that of potassium. It will be remembered that sodium and lithium form salts which may crystallize with 2 and 3 molecules of water, respectively. Hence we may assume that the increase in volume of the sodium and lithium ions, due to the formation of a relatively large hydrate, decreases the velocity of those ions to a far greater extent than the slight hydration of the large potassium ion decreases the velocity of that ion.

The atomic volume of lithium is about one-half that of sodium, and the maximum amount of water with which lithium salts crystallize from solution is 3 molecules, whereas the maximum for sodium salts is 2 molecules. Since the ratio of 2:3 represents approximately the ratio of the hydrating power of the two ions in solution, we should expect the effect, upon the velocity, of the greater increase in the volume of the small lithium ion, due to its hydration, to compensate somewhat for the smaller increase in the volume of the larger sodium ion. Experiment shows that the migration velocities are nearly equal.

The same relation holds for the metals of the alkaline earth group. The atomic volumes increase with increasing atomic weight. The migration velocities of the cations cal-

cium and strontium, whose salts crystallize with 6 molecules of water, are approximately equal to that of the barium cation, whose salts crystallize either with 2 molecules of water, or water-free. On the other hand, the magnesium cation, which has one-half the atomic volume of the calcium ion, has nearly the same migration velocity, due to compensation between the atomic volumes and the hydration of the ions.

The calcium ion has a slightly greater atomic volume than sodium, yet, owing to its much greater hydrating power, its migration velocity is considerably less.

The cations of copper, cobalt, and nickel have nearly the same atomic volumes and the same hydrating power. We should expect them to have the same migration velocity, and such is the case.

The atomic volumes of the halogens, chlorine, bromine, and iodine, are approximately the same. If their ions are hydrated we should expect them to combine with the same amount of water, and, therefore, they should give migration velocities of the same order of magnitude. This has been found to be the case. The atomic volume of fluorine has not been determined, but from its position on the migration velocity curve we should infer that its atomic volume is smaller than that of the halogens, and that its ion possesses a considerable degree of hydrating power.

Further, it will be noted that the migration velocities of the halogens are almost identical with those of the alkalis standing next above them in order of atomic weights, whereas their atomic volumes are very much smaller. This leads us to believe that the compensation, which brings about an equalization of the migration velocities of the two groups, is due to the increase in volume of the alkali ions by hydration.

The silver ion alone of all the metallic elements for which satisfactory data can be found presents an exception. It has a small atomic volume, and its salts crystallize from solution without water. We should expect it to have but slight hydrating power in solution and it should, therefore, have a high migration velocity, but this has been found to be slightly less than that of the halogens.

According to the law of Raoult, the lowering of the freezing point of a given weight of solvent by a dissolved substance is directly proportional to the amount of the substance dissolved, providing that substance is a non electrolyte. In the case of electrolytes the lowering produced by gram molecular weights of the dissolved substances are greater than those produced by gram molecular weights of non-electrolytes. This abnormality in the case of electrolytes is explained by the fact that an ion and a molecule lower the freezing point to the same extent.

The fact is that the freezing point method gives us a relation between the amount of solvent acting as such and the number of dissolved particles, whether they are molecules or ions.

Having determined the freezing point lowering for any concentration of a given electrolyte, it is an easy matter to calculate the amount of dissociation. For binary electrolytes α is obtained from the expression $\alpha = i - 1$, where i is the van't Hoff i . For ternary electrolytes, $\alpha = \frac{i-1}{2}$, and for quaternary electrolytes $\alpha = \frac{i-1}{3}$.

We have calculated the values of α from the molecular lowerings of all the solutions studied, for the dilute solutions up to the concentration at which the molecular lowering passes through a minimum. Beyond this concentration the molecular lowering of the freezing point increases, due to hydration, and, consequently, the calculated dissociation would increase. For that reason the values of α have not been calculated.

In the case of every salt studied, without exception, *the dissociation as calculated from the freezing point lowering is higher than the dissociation as calculated from the conductivity measurements.*

This will be seen by comparing the values obtained for α in the tables representing the freezing point and conductivity measurements for each salt.

If there were no hydration, these values should be equal. Since the freezing point measurements give us the most ac-

curate relation between the amount of the actual solvent and the number of dissolved particles, it, therefore, must give us the most accurate measure of the dissociation, when hydration is taken into account.

The conductivity of a solution is, as we have seen, dependent upon the number of ions present, their velocity, their mass and volume, and the viscosity of the solution. Since the temperatures at which the dilute solutions freeze are approximately only one-fourth of a degree or less below the freezing point of pure water—the temperature at which the conductivity measurements were made—we must conclude that the number of ions present and their velocities are in the two cases the same. Similarly, the viscosity of the solutions is the same in both measurements and, therefore, the friction between solvent and ion will vary directly as the surface of the latter.

We have shown that most metallic ions in solution have great hydrating power, and that the degree of hydration varies inversely with the atomic volume of the ion. Those ions which have the greatest hydrating power are those which have the smallest atomic volumes, and should, therefore, if there were no hydration, meet with less friction in their movements through the solution. They should have greater migration velocities, while exactly the opposite results are found.

A comparison of the values of α for a dilute solution of the strong acids shows that the dissociation as measured by conductivity is greater in every case than the dissociation measured by the freezing point method. In the more concentrated solutions the observed freezing point lowerings are higher than the molecular lowerings calculated from conductivity. This is due to the fact that the molecules or ions of those acids have considerable hydrating power, and we obtain in concentrated solutions results of the same character as with the salts.

Summary.

1. The freezing point lowerings and the conductivities of solutions of a number of electrolytes, over a wide range of concentration, have been carefully redetermined.

2. We observe that the molecular lowerings of the freezing point of all the electrolytes studied passes through a very pronounced minimum at concentrations ranging from 0.1 to 0.25 normal. The molecular lowerings calculated from the dissociation, as measured by conductivity, decrease regularly from the most dilute to the most concentrated solutions.

3. The magnitude of the molecular lowerings produced by molecular quantities of different salts varies directly as the number of molecules of water with which those salts crystallize from solution. The magnitude of the hydrating power of salts in solution is, in turn, proportional to the amount of water of crystallization.

4. That the ions have very great hydrating power is shown by the values of M and H for the different salts. The total amount of combined water decreases with increase in concentration, passes through a minimum, and then increases regularly with increase in concentration. The amount of water held in combination by one molecule of a salt is very large in the more dilute solutions where the ions predominate. It decreases rapidly with decrease in dissociation, and approaches a constant value at greater concentration.

5. The hydrating power of a salt is, primarily, a function of the cation. The results show that two salts which crystallize with the same amounts of water of crystallization and contain a common cation exhibit hydrating power of the same order of magnitude.

6. It has been found that the hydrating power of a cation is an inverse function of its atomic volume. Those cations which have the smallest atomic volumes have the greatest hydrating power, and *vice versa*. We may state the relations thus: *The hydrating power of the ions is an inverse function of their atomic volumes, and a periodic function of their atomic weights.*

7. Furthermore, we have found that those cations which have the greatest migration velocities exhibit, also, the smallest hydrating power, and *vice versa*. This probably accounts for the apparent anomaly which exists in the relation between the migration velocities of the ions and their atomic weights and atomic volumes. The influence upon the migration

velocity of the hydration of those ions with small atomic volumes is greater than that of the small hydration of those ions which have large atomic volumes.

8. In the case of every salt it has been found that the dissociation in the dilute solutions, as measured by the conductivity method, is *less* than that calculated from the freezing point lowering. Since the freezing point and conductivity measurements of the dilute solutions were made at approximately the same temperature, the number of the ions present, their velocities, and their hydration are practically the same in both cases. The solutions have, likewise, the same viscosity. Therefore, the friction between the solvent and ion will vary directly as the surface of the latter. This being the case, the greater the dilution, the greater will be the complexity of the hydrate, and, consequently, its surface. We should expect to find, therefore, a greater abnormality in the dissociation, as measured by the two methods, the greater the dilution at which the measurements are made. The results show this to be the fact.

It is only in case of those salts which crystallize in the anhydrous condition that we obtain comparable values for the dissociation, as measured by the two methods. These values are found only in those concentrations which lie close to that concentration which gives the minimum molecular lowering.

BIOGRAPHY.

James Newton Pearce, the author of this dissertation, was born in Oswego, Illinois, December 21, 1873. His early education was obtained in the public schools of his native village. In 1891, at the age of 17, he entered the Academy of Northwestern University, at Evanston, Ill., where he completed his preparation for college. In 1892 he matriculated in Northwestern University, graduating in 1896 with the degree of Ph.B., and the following year he took his Master's degree in Chemistry from the same institution.

From June, 1897, to January, 1900, he was head chemist for James S. Kirk & Co., soap manufacturers at Chicago, Ill. In January, 1900, he entered Chicago University to pursue graduate work in chemistry. In September of the same year he was appointed Instructor in Chemistry and Physics in the La Salle-Peru Township High School at La Salle, Ill., where he remained for two years. In 1902 he was appointed Instructor in Chemistry in Northwestern University and remained there until 1905, when he entered Johns Hopkins University as a graduate student in Chemistry. His subordinate subjects were Physical Chemistry and Physics.

